EVERYDAY CHEMISTRY

W. ROBINSON

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SIR HUMPHREY DAVEY, BART.
1778-1829
From an engraving by S. W. Reynolds after the painting by T. Phillips, R.A.

EVERYDAY CHEMISTRY

BY

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PREFACE

MY only apology for entering upon this work is the need I felt for some new method of approach to the subject of Chemistry, on being asked to conduct the Science side of the Officers' School of Education formed in the University of Oxford. A number of officers (most of them graduates in Science) were coming up continuously for monthly periods to discuss methods of presenting scientific subjects to a portion of the vast army of two million men. The task was entirely new, and for this reason alone the difficulties were great. New demands had been made and new methods had to be sought to meet those demands.

It was obvious from the start that, so far as advanced students were concerned—as well as those studying for such definite examinations as Matriculation—the old systematic method of presenting the subject could be followed. The interest was already created in the pupil—there was an end in view, and no danger of any slacking off. If this were so, then textbooks were numerous, and the instructors attending the school were all well qualified to deal with these pupils—or, if not, could not hope to gain sufficient grounding in one month to do so.

But there was the further problem of creating an interest in the minds of the large majority of men who had no

reason for studying Chemistry, or, in fact, any other subject, and who had no previous training in science. Obviously these men could not be treated as children —the same line of approach would not serve; and certainly any attempt at systematic study would create an interest in few only. Consequently, a method of approach along three main lines was adopted in the school:

1. History.
2. Common Objects.
3. Industrial Interests.

This method has been embodied in the present book.

The book is essentially a teacher's book, and is not intended to be used as a textbook by pupils working alone, though it is hoped it will prove interesting and useful as a pupil's book, under the guidance of a skilful teacher. Where formulæ and instructions with regard to experiments, or hints on the procedure of teaching, are given, they are solely for the use of the teacher, and should be used by the pupil at the teacher's discretion. In fact, the book may serve to teach Chemistry without the use of a single formula. At the end of each chapter a section marked "Results" is given, merely as a guide to the teacher with regard to the ideas, processes, and substances to be emphasized. In this way the teacher will be able to draw on his own fund of knowledge to amplify any facts given in the book.

Adult education does not cease with the Army Scheme. It is a growing problem, and will develop enormously under the new Education Act. It is hoped this book may prove of use not only in Continuation Schools, but

in Study Circles and W.E.A. Classes, where men are inquiring as to the "ways of science," and teachers are troubled, not with the mere imparting of knowledge, but with the greater problem of how to use their subject as an educational instrument.

It is not beyond hope that the book may form the basis of an introduction to Chemistry in junior schools also. Such a treatment of the subject might easily form the groundwork on which to build more systematic study in preparation for examinations.

In conclusion, I wish to thank all those officers—many of them Science masters in our Public and Secondary Schools—who by their suggestions and discussions are mainly responsible for the framework of this book.

W. ROBINSON

OXFORD.

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EVERYDAY CHEMISTRY

CHAPTER I

WATER

1. Occurrence

The fact that water exists in such large quantities on this planet, and in its liquid state, makes possible not only the existence of plant and animal life, but the formation of the earth's crust as we now know it is itself largely dependent upon the existence of water. Without it life would fail and the earth become as some other planets. Moreover, the earth's very shape and configuration would disappear. The fact that hydrogen, which is abundant throughout the solar system, should be combined in definite proportion with oxygen in such enormous quantities, when in itself, or in combination with other elements, or in combination with oxygen in other proportions, it would cease to serve any useful purpose from the point of view of life, is in itself one of the wonders of Nature. The full secret of the matter cannot even be laid at the door of chemical affinity, but still remains profound. That which seems common and easily obtained is in itself one of the greatest wonders of our earth.

Practically five-sevenths of the earth's surface is composed of water in sea, lakes, and rivers. A glance at the two hemispheres, land and water, will show this.

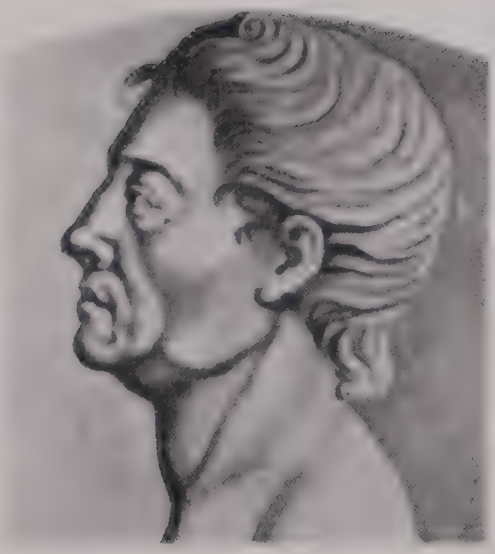
But this is not the total water in the globe. A large number of rocks in the earth's crust are crystalline in character, and many of them contain water of crystallisa-

tion. Plants are largely composed of water, and take most of their food in the form of solutions, the water ascending and descending in the stem during the greater part of the year. We ourselves are largely water, and an analysis would show a 70 per cent. yield. It is interesting to note that a large amount of water in the world is continuously running uphill. This is true in the case of the water in plants, also all rivers running towards the equator, for the land around the equator is a mountain, seventeen miles high. We are accustomed to regard water as always running downhill, failing to regard other forces which may be at work, such as capillary action.

If we regard water as only existing for the preservation of life we fail to see the wonderful romance written in the discoveries of the nineteenth and twentieth centuries. For centuries it has been a means of transport, and has played an important part in the destinies of nations both as a barrier and as a means of communication. The discoveries both in the old and new worlds have been largely the result of river transport. But not until the end of the eighteenth century did man—except in a few isolated cases—seek to harness the great powers which water is capable of displaying. The resulting years have seen the development of steam power of all kinds, hydraulic power and the production of electricity by turbines. It only remains now to harness the great forces contained in the tides. No serious attempt has yet been made. As an enemy water is irresistible, defiant, but when trained and directed it becomes the most useful servant of man.

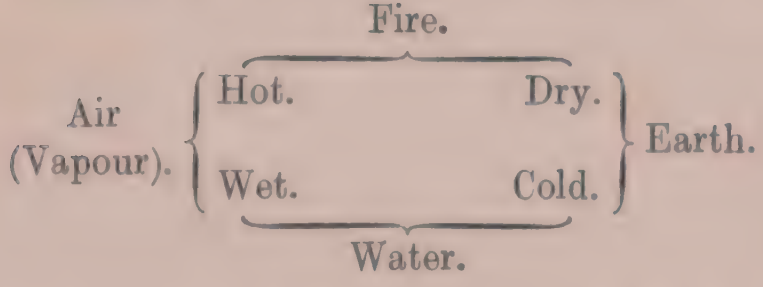
2. History

It is interesting to note that the bulk of our modern chemistry only began to be formulated during the eighteenth century, and indeed its beginnings cannot be



traced farther back than the middle of the seventeenth. Then the chemists threw off the cloak of alchemy and magic, ceased to inspire a fear of Nature, and began to love her. Since that time she has revealed herself to her lovers with a readiness beyond measure, and the leading chemists have been true Nature students.

The ancient Greeks had four elements which they considered to be the direct result of the combination of the four properties supposed to exist in Nature. Thus:



This conception of the four elements lived until the time of Boyle, and is found in all our literature prior to the middle of the seventeenth century—pre-eminently in Shakespeare and the Bible. Boyle, in his "Sceptical Chemist," was the first really to attack this doctrine, but his chief work was done on Air.

It was not until a century later that any real work was done on Water. About 1770 Priestley was busy in this country experimenting. He was not a good experimenter, paying too little attention to detail, and indeed had very little system in his work, believing largely in the chance of a result. In this way, about 1774, he had discovered oxygen (fire air) probably by heating red lead.

$$2Pb_3O_4 \longrightarrow 6PbO + O_2.$$

Hydrogen was known, and had been since the time of Paracelsus, 1493-1541. Priestley had discovered that

oxygen and hydrogen, when mixed in certain proportions, explode. He was very fond of doing this as a trick experiment in ladies' drawing-rooms, and was in great demand. One day his assistant, Warltire, noticed the formation of water, and pointed it out, but Priestley did not realize that there was any connection. Cavendish (1731-1810) burnt hydrogen against a cold surface and produced water, but he failed to reap the benefits, being a firm believer in the phlogistic theory (see Chapter III.). Priestley was informed of Cavendish's work and refused to believe it. He performed the same experiment and produced no water, probably because he burnt CO (carbon monoxide) instead of hydrogen.

Lavoisier (1743-1794), the father of modern chemistry, was the first to really prove the constitution of water; but this he probably did because of the suggestion made by Cavendish. He had the power not only of devising and conducting experiments, but of assimilating those of

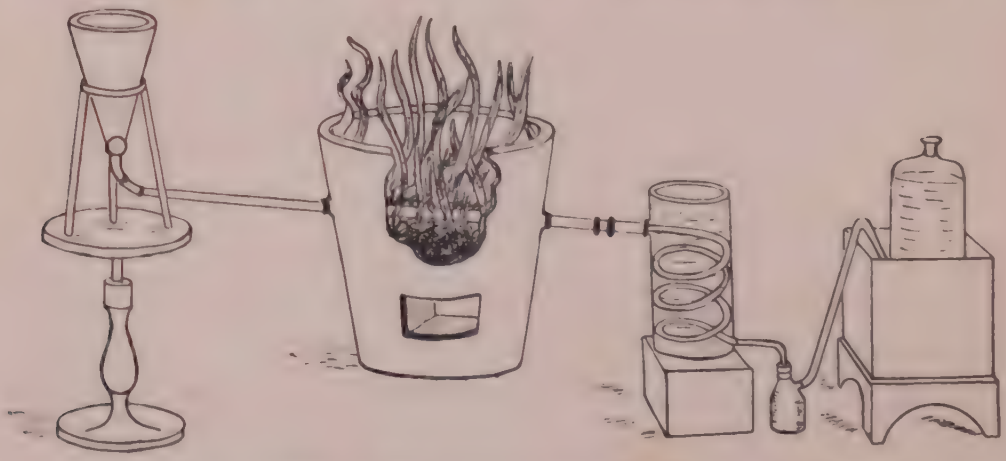


FIG. 1—LAVOISIER'S EXPERIMENT FOR SPLITTING UP WATER

others, and deducing from them their correct significance. In 1782 he repeated Cavendish's experiment on a large scale, and found the proportions of oxygen and hydrogen to be 1 to 1·91. Not long afterwards he split up water by passing steam over iron wire heated in a porcelain tube.

Thus the constitution of water was established. It had been suggested by James Watt, the inventor of the steam engine; but it was only established by the successful work of Lavoisier, assisted by Blagden.

3. Analytic Experiments

(A) *Lavoisier's Experiment*—Pass steam over red-hot iron filings.

$$3Fe+4H_2O \longrightarrow Fe_3O_4+4H_2.$$

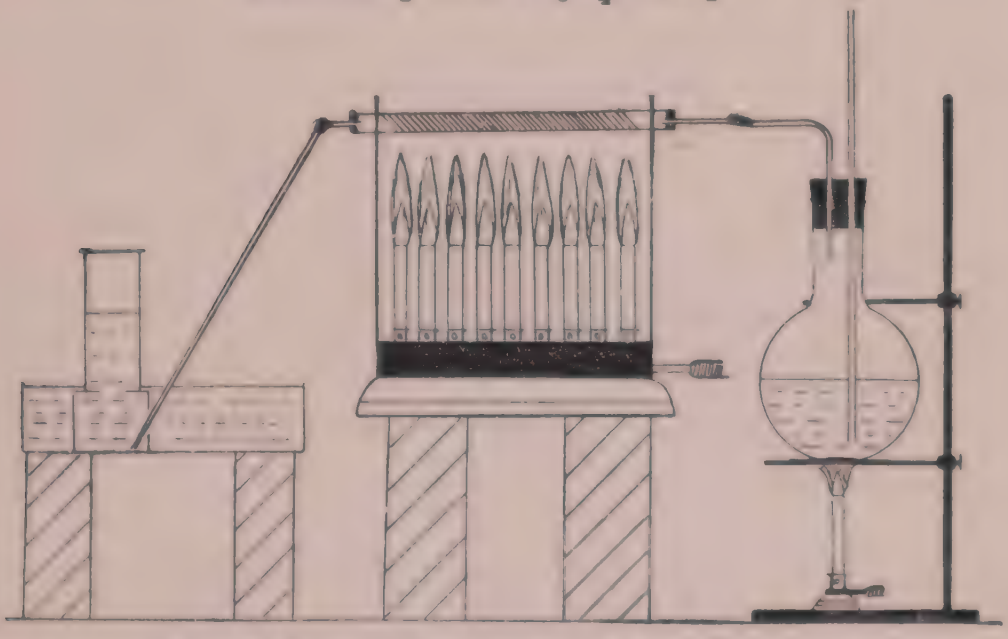


Fig. 2.—Passing Steam over Red-Hot Iron

The operation can be explained by stating that iron in a red-hot condition is more powerful to attract oxygen than hydrogen is, and thus wins in the fight, setting free the hydrogen.

The properties of hydrogen can be tested and explained.

(*a*) Burns with a blue flame.

(*b*) Puts out a taper.

(*c*) Not soluble in water.

(*d*) Explodes when mixed with air.

(*e*) Lighter than air—soap-bubble rises; can be poured from lower to upper jar.

The name Hydrogen, being fairly familiar, should be introduced instead of "Inflammable Air," which leads to confusion; but in introducing it the meaning should be explained by reference to many other words containing the same root.

Hydor = water; gennao = to produce.

This word was coined by Cavendish, in 1776, from the above Greek words.

N.B.—Care should be taken to use a hard glass tube, and to see that the tube is hot before steam passes over. Also, when the heat is taken away from the flask the gas outlet tube should be removed from the water.

(B) *Electrolysis*—This experiment is very convincing, and can be fitted up simply as shown. Direct current from a lighting system can be used if run through a resistance lamp; or a couple of Leclanché cells will do.

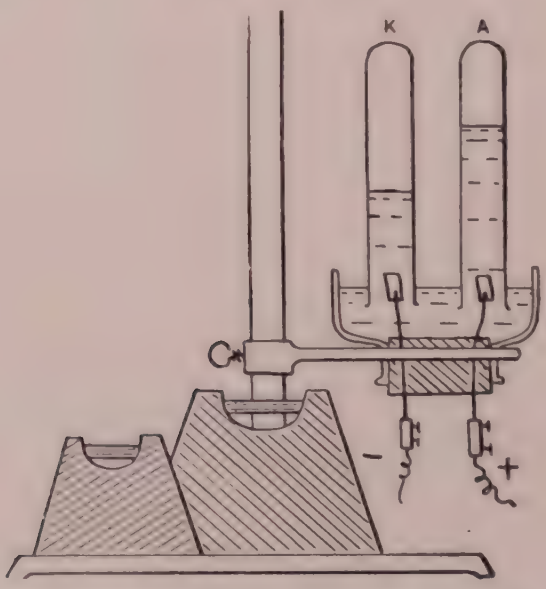


Fig. 3—Electrolysis of Water

Alluminium terminals are quite as effective as platinum, but the experiment should be allowed to run previous to the lesson, and then the test-tubes refilled with water if it is desired to obtain a good effect quantitatively.

(C) *Sodium on Water*—First show the action by floating a piece of sodium on a filter paper. The hydrogen burns. To collect the hydrogen, wrap the sodium in filter paper and bind by wire, holding it under water by the wire. Place a test-tube on top. This method is absolutely safe.

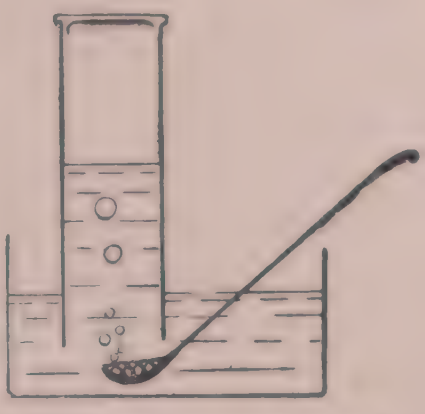


FIG. 4—SODIUM UNDER WATER

The combination can be explained by stating that sodium is a substance which is fond of both hydrogen and oxygen, but likes them in equal quantities. Thus the odd hydrogen is given off, and if free burns owing to the heat generated by the combination.

$$2H_2O + Na_2 \rightarrow 2NaOH + H_2.$$

Test the hydrogen produced.

4. Synthetic Experiments

1. *Cavendish's Experiment*—Burn hydrogen against a cold surface and produce water.

Where does the oxygen come from?

2. *The Eudiometer*—Explode O (oxygen) and H (hydrogen) in proportion of 1 to 2, and show that no gas remains.

3. *Priestley's Experiment*—Explode O (oxygen) and H (hydrogen) in a soda-water bottle. This is quite safe when the bottle can be guaranteed; but it should always be held in dusters, and the mouth of the bottle must never be pointed towards anyone, as a tongue of flame about a yard in length is usually emitted.

4. *Hydrogen over Copper Oxide*—

$$2CuO + 2H_2 \rightarrow 2H_2O + Cu_2.$$

This experiment is performed in the same way as passing steam over red-hot iron, using a hard glass tube. Show the copper in the tube at the conclusion, and explain simply what has taken place.

5. Natural Waters

1. *Suspension*—Introduce the idea of suspension and filtration. Refer to various filters.

(*a*) House filter by charcoal. Show the action of charcoal on colour, smell, and suspended matter.
(*b*) Filter paper.
(*c*) Sand and gravel filters on a large scale.

If possible, visit a waterworks and see the process working.

2. *Solution*—Refer to sugar in tea, salt in water, and show various solutions. Refer to evaporation in Nature—salt on the seashore and desert. Show evaporation. The solution of solid matter in water gives it its taste. Refer to taste of rain, and allow to taste distilled waters. A few figures may be given as to solid matter in water—not with view to memorizing them, but to emphasize the facts.

	Manchester		Another Town	
	Parts per Million	*Grains per Gallon*	*Parts per Million*	*Grains per Gallon*
Total solids	63	4·4	530	37·1
N_2 as nitrite and nitrate	·25	·017	7·8	·546
Free NH_3	·03	·002	·063	·303
Albumenoid NH_3.. ..	·07	·005	·9	·063
Chlorine	11·4	·8	69	4·8
Temporary hardness ..	—	·1	—	7·2
Permanent hardness ..	—	2·4	—	14·4

Some reference should be made to medicinal waters.

The problem of gases dissolved in water should be touched, not as a bare fact, but the whole relationship it has to the existence of life. The following figures of Thames water show very clearly how the Thames acts as a reservoir for both carbon dioxide and nitrogen when these are in excess owing to excessive population and factories. The small proportion of nitrogen dissolved at Erith may be due to the existence of allotments producing plants of the pea family, which have the property, by the aid of bacteria, of absorbing free nitrogen from the air.

	Kingston	*Hammer-smith*	*Somerset House*	*Green-wich*	*Wool-wich*	*Erith*
CO_2	30·3	35·6	45·2	55·6	48·3	57
O_2	7·4	4·1	1·5	·25	·25	1·8
N_2	15	15·1	16·2	15·4	14·5	15·5
$O_2 : N_2$ ..	1 : 2	1 : 3·7	1 : 10·5	1 : 60	1 : 52	1 : 8

Normal Ratio, 1 : 1·8

3. *Crystals.*—The production of crystals should be shown, wire baskets, etc., being covered with alum and other crystals; but the effect of this phenomenon should be shown on the crystalline rocks of our earth's surface, many of which are the result of solution.

6. Summary

1. *Occurrence*—Five-sevenths earth's surface; rocks; plants; 70 per cent. man.

2. *History*—Water as an element. Priestley exploding H and O. Warltire noticed water. Cavendish burnt H and noticed water formed. James Watt suggested constitution. Cavendish, believer in phlogiston theory.

failed to reap fruits of investigation. Lavoisier heard of it and split up water. Also built it up.

3. *Analytic Experiments*—

1. Steam over red-hot iron, $3Fe+4H_2O \rightarrow Fe_3O_4+4H_2$.
2. Electrolysis.
3. Sodium on water, $Na_2+2H_2O \rightarrow 2NaOH+H_2$.

4. *Synthetic Experiments*—

1. Burn hydrogen against a cold surface.
2. Eudiometer.
3. Explode O and H in soda-water bottle.
4. Pass H over CuO.

$$2CuO+2H_2 \rightarrow 2H_2O+Cu_2.$$

5. *Natural Waters*—Suspension; solution; filtration and distillation; crystals.

7. Results

(A) *Ideas*—

1. Compound.
2. Element.
3. Combination; some idea of chemical affinity.
4. Suspension; filtration.
5. Solution; crystallization.

(B) *Substances*—

1. Hydrogen.
2. Oxygen (acid producer).
3. Water a definite compound unlike either.
4. Iron and its oxide.
5. Sodium.
6. Copper and its oxide.

CHAPTER II

AIR

1. History

LIKE water, air was one of the four elements of the Aristotelian philosophy, and was so regarded until the work of Boyle and Mayow in the seventeenth century. Boyle may be regarded as the first real chemist as distinct from the alchemists. He was largely instrumental in forming the Royal Society, and in 1680 became its President. In his work he was aided largely by Mayow. It is unfortunate that Mayow died in 1679, aged only thirty-four. If he had lived, chemical thought would have been advanced a century.

One of the first experiments was that of burning a candle in an enclosed space. The simple fact that the candle went out led these two chemists to conclude that:

Either (1) The candle took something from the air essential to combustion; or (2) it formed a poison which put out the flame.

They then proceeded to burn sulphur in an enclosed space over water by means of a burning glass, and noted the rise of the water. This led them to decide that their first conclusion was correct, and they divided air into two parts:

1. Fire air.
2. Foul air.

This was a remarkable advance, and led to the writing of the "Sceptical Chemist" by Boyle, in which he at-

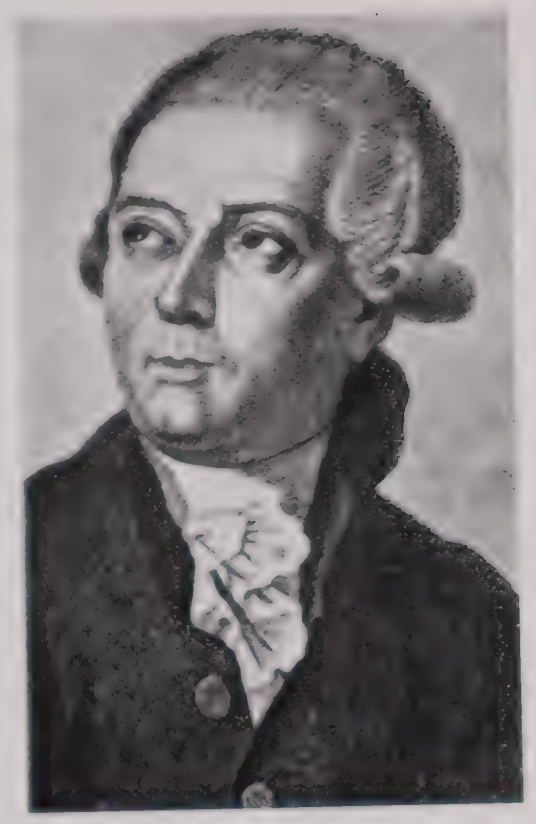
tacked the doctrine of the four elements so strongly advocated by the Paracelsians. The book was first published in 1661, and led to much discussion; but its conclusions were not generally accepted for another century. The simplicity of its style, however, did much to dispel the mysticism of the alchemists.

At this time everyone believed in the phlogiston theory, which in effect said that all substances were formed of a calx and phlogiston—an ethereal substance which escaped when bodies burnt. This belief in the phlogiston theory was responsible for retarding chemical discovery to a very great extent. In 1630 Jean Rey had discovered that the calx of a metal was heavier than the metal. But this did not deter the ardour of many chemists for the phlogiston theory—they merely said that phlogiston had negative weight. Under the skilful hands of Lavoisier, however, the theory was soon to receive its death-blow.

Since the discovery that air consisted of two parts a search had been going on in the chemical world for "fire air." This was not discovered, however, until 1774, when, working independently, it was produced by Scheele, a Swede, and by Priestley, who communicated his results to Lavoisier.

Lavoisier's experiment is the most important from the point of view of the advance of chemical thought, and when we consider the dominating ideas of the time and the scanty apparatus available it is perhaps the most marvellous piece of chemical research ever conducted.

Lavoisier heated mercury in an enclosed space of air connected with a mercury trough, and showed the rise of mercury and the formation of the red oxide. He also produced oxygen from the oxide so formed, and showed that this oxygen added to the "Foul Air" produced the original volume.



This led to the final rejection of the phlogiston theory, and the belief that air contained oxygen, which oxygen was largely responsible for the processes of combustion.

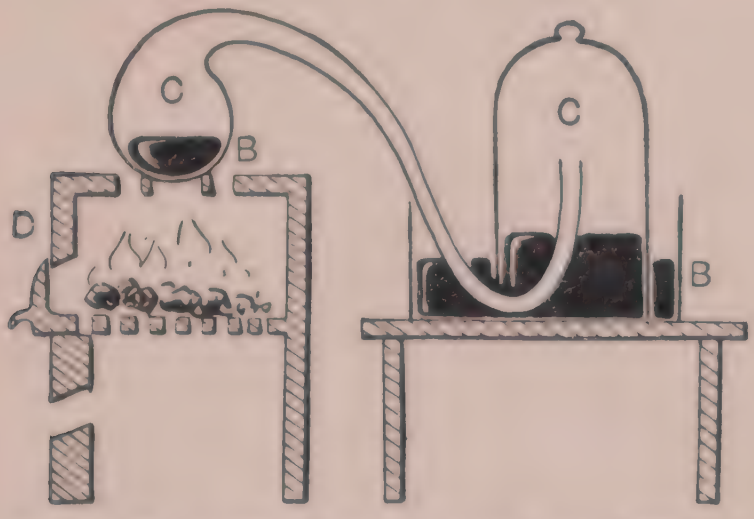


FIG. 5—LAVOISIER'S EXPERIMENT WITH MERCURY
B = mercury; C = air; D = furnace

2. Extraction of Oxygen

1. Heat iron, copper, magnesium, and show the formation of the oxide. Perform this experiment quantitatively by heating copper in a crucible.

Why does the copper increase in weight ?

Where does the added substance come from ?

Refer to the slow rusting of iron and metals in general.

2. Candle burning in an enclosed space. Why does the candle go out ? Refer to Boyle and Mayow's conclusions.

3. Burn phosphorus over water, marking the height of the water before and after in the bell-jar. The phosphorus is best supported on a crucible lid, which has been inserted in a cork. Unless it is desired to obtain a good quantitative result the pressures need not be equalized at the end of the experiment. Test the remaining air. Note that its properties are negative.

A better result can be obtained by the slow rusting of iron filings in a moist muslin bag, or the slow oxidation of phosphorus. Phosphorus takes a few days, and iron filings may take two weeks to complete.

FIG. 6—SLOW OXIDATION OF PHOSPHORUS

5. Oxygen can be extracted from the air by pyrogallic acid in the presence of potassium hydrate. Invert a test-tube over a mercury trough, having first put into the test-tube some pyrogallic acid. Then, by a pipette, insert into the tube some caustic potash. Remove the tube, and shake well; then replace over the bath, and the mercury will rise one-fifth of the way up the tube.

6. Pass air over heated copper. The hard glass tube must be well packed with copper and the air passed over slowly, and nitrogen will then be collected free from oxygen.

7. *Lavoisier's Experiment*—Heat mercury in an enclosed

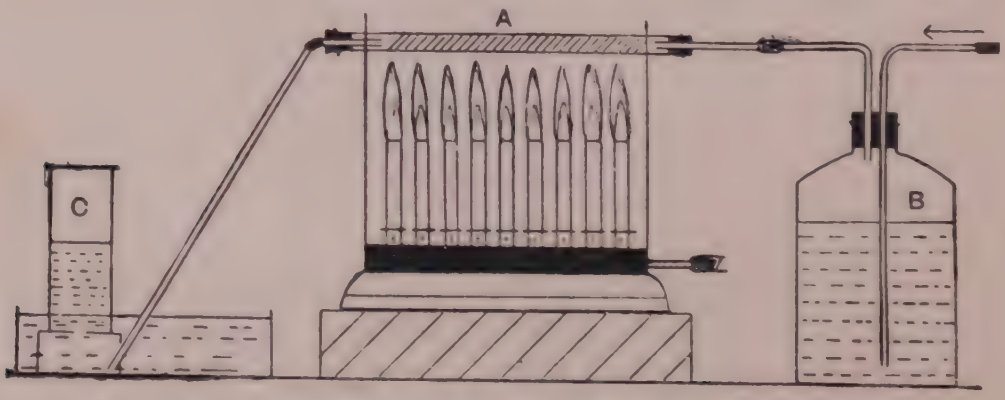


FIG. 7—PASSING AIR OVER HEATED COPPER

space connected to a mercury trough, and note the rise of the mercury and the formation of the oxide. This ex-

periment will take about two weeks to complete on a small scale.

3. Production of Air and its Gases

1. Produce oxygen from the following substances:

(*a*) $2Pb_3O_4 \longrightarrow 6PbO + O_2$ (red lead).

(*b*) $2KNO_3 \longrightarrow 2KNO_2 + O_2$ (potassium nitrate or nitre).

(*c*) $2HgO \longrightarrow Hg_2 + O_2$ (mercuric oxide).

2. Burn in air and then in oxygen such substances as the following: Magnesium, sulphur, charcoal, iron. This leads up to the idea of oxygen as undiluted air. What is the effect of oxygen on life? Why is oxygen given to dying people? What part of the air do we retain in breathing?

3. Introduce oxygen to nitrogen in the proportion of one-fifth to four-fifths. The nitrogen extracted from the air in a previous experiment may be used. Note that there is no visible change, no heat evolved or required, and that the resulting mixture acts like air in every way.

4. Pass a continuous electric spark through a globe of air and note brown fumes of N_2O_4 (nitric oxide). Note its smell, and that it is readily absorbed by potassium hydrate:

$$N_2O_4 \text{ (nitric oxide)} + 2KOH \longrightarrow KNO_3 + KNO_2 + H_2O.$$

Note its acrid smell, and compare with that observed during a thunderstorm. Why does the action cease when a small proportion only of nitrogen and oxygen have united? It is a reversible reaction, and N_2O_4 is easily decomposed by an electric spark. The action should therefore be represented thus:

$$N_2 + 2O_2 \rightleftharpoons N_2O_4.$$

Note the meaning of this with regard to natural pheno-

mena. If this were not a reversible reaction a single flash of lightning would turn the whole atmosphere into this gas. Note that the gas is easily soluble in water, and produces an acid (turning blue litmus red).

$$N_2O_4 \text{ (nitric oxide)} + H_2O \rightarrow HNO_3 + HNO_2.$$

These properties show that a substance has been produced totally different from either oxygen or nitrogen, whereas air has the properties of oxygen diluted by those of nitrogen.

Moreover, air can be produced by simply mixing oxygen and nitrogen, and there is no display, whereas this compound requires heat developed by an electric spark.

Refer to water, also formed from two gases, but differing entirely from either. Air is a mixture, whilst water is a definite chemical compound.

4. Carbon Dioxide

1. *Respiration*—What happens if a number of people are shut up in a small room without ventilation? What happened in the Black Hole of Calcutta, and in several German prison camps? What are persons taking out of the air? What do they give out?

(*a*) Pump some air into lime-water.
(*b*) Now breathe into the lime-water, and note the difference.
(*c*) Burn a candle in a closed space and test by lime-water.
(*d*) Keep a plant in an enclosed space and note the formation of this gas, and that the plant dies.
(*e*) Allow vegetable matter to decay in a bell-jar, and note the same gas is formed.

This gas is formed continuously by the breathing of

animals and plants, by combustion, and by decaying vegetable and animal matter. It is poisonous when in excess. The normal amount is 4 parts in 10,000 in the atmosphere. Its presence is necessary to many operations, such as the rusting of iron, the dissolving of rocks in water, the setting of mortar, the breaking up of rocks; but in excess it is dangerous to life. How, then, is its proper proportion regulated?

2. *Regulation of* CO_2 *in the Atmosphere*—(1) Enclose a plant in a bell-jar in water and expose to the sunlight. Note small bubbles of gas forming on the leaves and rising to the surface. Test the gas, and see that it is oxygen.

Perform the same experiment by night, and note that CO_2 (carbon dioxide) is given off and not oxygen.

Plants are the first purifiers of the atmosphere. It was thought that by night plants breathed as we do—that is, took in oxygen and breathed out carbon dioxide; and that by day they performed the opposite operation—that is, breathed in carbon dioxide and breathed out oxygen; but this is not the case. If it were so, a plant would be able to live its days in an atmosphere of carbon dioxide. This is very difficult to test owing to the occurrence of night every twenty-four hours; but it is most improbable that a plant would thrive in such an atmosphere, and it can be shown that it is detrimental to the growth of the plant.

What happens is that the plant breathes as we do, but that under the action of sunlight the chlorophyl (the green colouring matter of the leaves) is able to split up carbon dioxide into carbon monoxide and oxygen.

$$2CO_2 \longrightarrow 2CO + O_2.$$

This operation is a most difficult one to perform in the chemical laboratory, but is being silently performed by Nature daily in the plant world. It is from this carbon monoxide that the plant builds up, first, a substance known

as formaldehyde; then starch, and finally sugar. These processes we are still unable to perform in the chemical world, but Nature performs them without ostentation.

$$CO+H_2O \longrightarrow CH_2{:}O \text{ (Formaldehyde)}+O.$$

This may represent the first stage of the plant's work. Formaldehyde is poisonous to the plant, so the molecule is multiplied, and we obtain—

$$\underset{\text{(starch)}}{(C_6H_{10}O_5)_n}+nH_2O,$$

and finally such things as $C_6H_{12}O_6$ (fructose), and $C_{12}H_{22}O_{11}$ (beet and cane sugar).

The process may, however, take place in the actual breathing out of carbon dioxide, thus:

$$CO_2 \text{ (carbon dioxide)}+H_2O \longrightarrow CH_2{:}O+O_2,$$

but in any case oxygen is given off. Thus plants are the first great purifiers of the atmosphere, and are absolutely essential to the lives of animals. In the order of creation, therefore, they came before animals, and, indeed, prepared the way for them. Why are plants carried out of hospital wards at night ?

2. Rocks also assist in purifying the atmosphere. Certain types of porous oolitic rocks absorb carbon dioxide in larger quantities than the other constituents of the atmosphere. Certain sandstones, like greensand, work in this way. The action on such stones of carbon dioxide is well exemplified in such buildings as the Radcliffe Camera, Oxford. Mortar is continually absorbing carbon dioxide, and so hardens.

$$CaO \text{ (Lime)}+CO_2 \longrightarrow CaCO_3 \text{ (Limestone)}.$$

3. The sea is a great purifier of the atmosphere, and acts like a reservoir for absorbing and giving up carbon

dioxide. Thus, if there is excess of carbon dioxide in the atmosphere the sea dissolves it, and if there is too little it gives some up. This action is not thoroughly understood, but it may be due to the formation of certain hydrogen salts of carbonic acid.

(*a*) $CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$.
(*b*) $Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NaHCO_3$.

5. Summary

1. *History*—Air as an element. Formation of calx. Mayow, 1660, divided into "fire air" and "foul air." Increase in weight on burning. Negative weight of phlogiston. Production of oxygen by Priestley and Scheele, 1774. Lavoisier's experiments with mercury.

2. *Extraction of Oxygen*—

1. Heat copper, iron, lead, magnesium. Do one quantitatively.
2. Candle going out; conclusions.
3. Phosphorus or magnesium over water.
4. Slow rusting of iron and burning of P.
5. Extraction of oxygen by pyrogallic acid + KOH.
6. Pass air over heated copper; collect nitrogen.
7. Lavoisier's experiment with mercury.

3. *Production of Air*—

1. Introduce oxygen to nitrogen $\frac{1}{5}$ to $\frac{4}{5}$.
2. Burning of metals in O. Oxygen as undiluted air. Air as a mixture.
3. Production of oxygen from Pb_3O_4, HgO, *Nitre*.
4. Fixation of nitrogen by electric spark. N and O in combination.

4. *Carbon Dioxide*—

1. Respiration; combustion; decay. Show presence by lime-water.
2. Action of plants, rocks, sea.

6. Results

(A) *Ideas*—

1. Mixture.
2. An oxide.
3. Chemical action in Nature.
4. Different rates of chemical action.

(B) *Substances*—

1. Nitrogen.
2. CO_2.
3. Magnesium and its oxide.
4. Phosphorus and its oxide.
5. Mercury and its oxide.

CHAPTER III

BURNING

1. History

ALL the four elements of Aristotle have been, and are to-day, worshipped. India to-day furnishes us with examples of the worship of fire, water, and earth. The Ganges is a holy river to nearly all native religions, and the "towers of silence," where dead bodies are hung to feed the carrion crow and vulture, are a testimony to the worship of the earth, which must not be contaminated by coming in contact with death. But "fire" has perhaps been more worshipped than either water or earth, probably because it has been more feared.

As shown in the first chapter, fire was one of the elements of the system of Aristotle, and so remained until the work of Boyle and Mayow. But the work of Boyle only led to the substitution of the phlogistic theory for the four element theory.

It had long been observed that certain substances possessed the property of "fire matter," and would thus burn. On burning, an ash was usually left, which was called cineres (ashes), or calx (lime). (Limestone had been burnt by the Romans, producing lime.)

Stahl (1660-1734) attributed burning to the escape of phlogiston, and of this substance he says: "It is a very subtle matter, capable of penetrating the most dense substances; it neither burns nor glows, nor is visible: it is agitated by an igneous motion, and it is capable of

communicating its motion to material particles apt to receive it. The particles when endued with this rapid motion constitute visible fire." Phlogiston, however, was a new name for an old idea. For long the work of spirits had been associated with fire, and many interesting customs still prevail, such as putting the poker in the form of a cross to the bars of a grate to make the fire burn.

The whole process of oxidation and reduction was explained by Stahl by the aid of this theory.

$$\text{Substance} \rightarrow \text{phlogiston} + \text{calx}$$

was the great underlying equation of these processes. It did not matter that Rey had discovered that the calx in many cases was heavier than the metal burnt: phlogiston probably had negative weight, and this would explain the phenomenon. This theory remained predominant until the work of Lavoisier, and then took ten years to finally die.

2. Early Investigations

The work of Boyle and Mayow has already been reviewed in Chapter II. They found that the air consisted of two parts, which they called " fire air " and " foul air," and that these were roughly in the proportion of 1 to 4.

John Rey had shown that a metal heated increased in weight, and this can be well shown in the case of copper heated in a crucible with a lid. The lid should be occasionally raised during the experiment.

A good experiment to demonstrate the fact that things burning increase in weight is the old one of a candle in a lamp-glass. The chimney should be filled with pieces of dry quicklime to catch the water and the carbon dioxide. This is much better than the two layers of calcium chloride and caustic potash.

What is happening here? Either (1) Phlogiston with negative weight is escaping, or (2) "fire air" is being taken up.

We have seen how the search for "fire air" was rewarded in 1774, but it was Lavoisier who finally dealt the death-blow to the phlogiston theory. By a study of the combustion of organic substances he concluded that:

1. Substances burn only in pure air.

2. This air is consumed in combustion, and the increase in weight is equal to the decrease in weight of the air.

3. The combustible body is, as a rule, converted into an acid.

Thus his theory can be expressed:

$$\underset{\text{(element)}}{\text{Metal}} + \text{oxygen} \longrightarrow \underset{\text{(compound)}}{\text{calx}}$$

$$\text{Calx} - \text{oxygen} \longrightarrow \text{metal.}$$

in contradiction of the phlogistic theory—

$$\underset{\text{(compound)}}{\text{Metal}} - \text{phlogiston} = \underset{\text{(element)}}{\text{calx}}$$

Lavoisier said, in 1783: "But if in chemistry everything can be satisfactorily explained without the aid of phlogiston it thereby becomes eminently probable that such a principle does not exist, that it is a hypothetical being, a gratuitous assumption, and sound logic is opposed to unnecessary complication."

3. Experimental

A series of experiments will now be performed, breaking down common notions with regard to burning, and leading up to the modern theory.

1. *Burning in Air and Oxygen*—Burn in air and oxygen such substances as sulphur, iron, charcoal, magnesium, phosphorus.

Note that in the case of the first three the substances

will scarcely burn in air, and that in all cases the action is more vigorous in oxygen. Note that substances are formed—either gases or ashes. Thus "fire air" or oxygen has something to do with most burning processes.

2. *Burn Substances in Chlorine*—Burn Dutch metal (fine copper), antimony, bismuth, sodium, and turpentine in chlorine. Dutch metal takes fire spontaneously; note that a white powder is produced. Powdered antimony and bismuth usually require slight heating. Sodium is usually described as explosive, but if melted first in a deflagrating spoon it burns easily, producing common salt. A filter paper soaked in turpentine burns spontaneously, with the production of carbon. Thus oxygen is not always essential to burning, but it may be the result of other chemical combination, and may be spontaneous.

FIG. 8—AIR BURNING IN COAL GAS

3. *Burn Air in Coal Gas*—This experiment can be simply performed by the aid of a lamp-glass, which should be fitted as shown.

Gas is sent in and lit at the top of the glass, and then, if a light is applied at the bottom of the air-tube, and if it be sufficiently short and dusted with chalk, the light will jump up to the top of the tube. Another way of lighting the air is to light the gas at the top of the glass and then turn off the gas current. When the top flame goes out the flame appears at the top of the air-tube, and the gas should immediately be turned on and lit at the top of the glass as before.

This shows that "combustible substance" and "supporter of combustion" are merely relative terms,

and that combustion is usually a union of two or more substances.

4. *Potassium on Water*—If a filter paper is floated on water and a piece of sodium or potassium is placed on it the metal bursts into flame. Thus water is not always a fire quencher. What is happening? The potassium is fond of two things in water, both hydrogen and oxygen, but likes them in equal quantities. Thus one, hydrogen, is set free. The heat developed in the union of the potassium, hydrogen, and oxygen is sufficient to set alight the odd hydrogen.

$$K_2 + 2H_2O \longrightarrow 2KOH + H_2.$$

5. *Burning Sugar by Water*—Mix some sugar with some dry sodium peroxide on a sand tray, and drop water on to the mixture as shown. The sugar burns violently

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2.$$

Here there is a splitting up of two substances, with the formation of two others—a kind of "general post"—

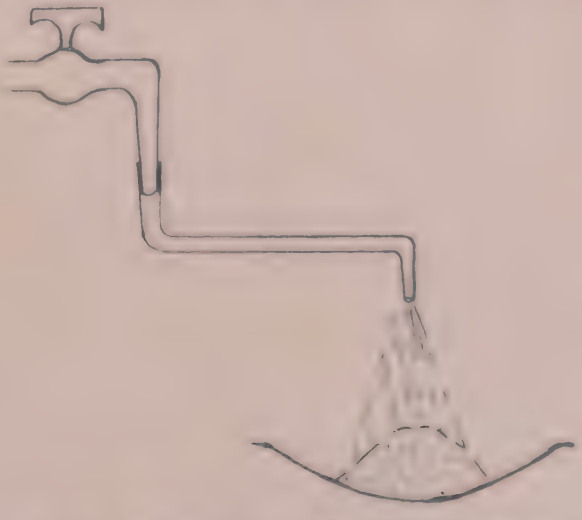


Fig. 9—Water on a Mixture of Sugar and Sodium Peroxide

the heat generated being sufficient to set the sugar on fire in spite of the presence of some water. Water may therefore cause fire, as in this case and the case of sodium.

6. *Burning under Water*—Take a beaker of water and drop in some crystals of potassium chlorate and a few pieces of phosphorus. Now pour down a thistle funnel a few drops of strong sulphuric acid, so that they come in contact with the potassium chlorate near the phosphorus. The beaker should stand on a white surface. It will be observed that the phosphorus burns under water.

This experiment is dangerous, and great care should be taken not to pour down too much sulphuric acid.

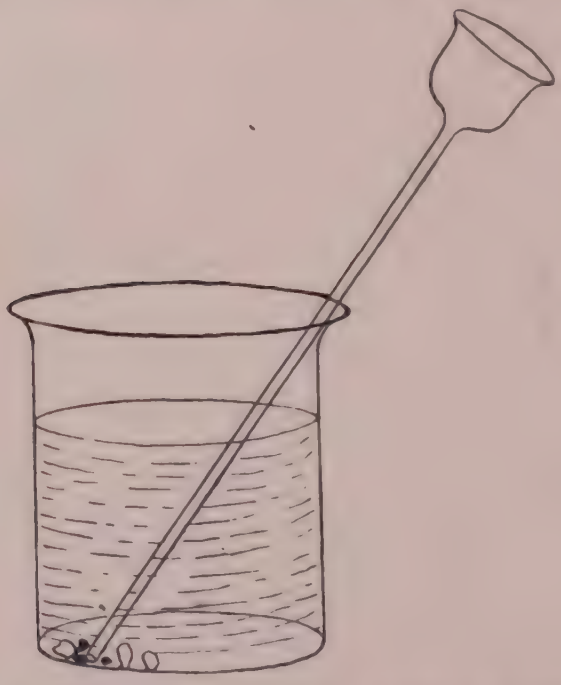


FIG. 10—PHOSPHORUS BURNING UNDER WATER

The probable reaction is as follows:

$$3KClO_3 + 2H_2SO_4 \longrightarrow KClO_4 + 2KHSO_4 + H_2O + 2ClO_2.$$

The ClO_2 (chlorine peroxide) is seen as a yellow substance.

Now ClO_2 splits up as follows:

$$2ClO_2 \longrightarrow Cl_2O \text{ (chlorous oxide)} + O_3 \text{ (ozone)}.$$

Oxygen, in the peculiar form of ozone, is thus produced, and this probably causes the phosphorus to burn.

Fire is thus seen entirely surrounded by water; and phos-

phorus, which ordinarily is kept in water to prevent it burning, now burns in contact with water.

7. *Spontaneous Combustion in Air*—Produce phosphine by the action of sodium hydrate on phosphorus.

Take a flask, and add by weight three parts of water and three parts of sodium hydrate and four parts of phosphorus. Connect the flask as shown.

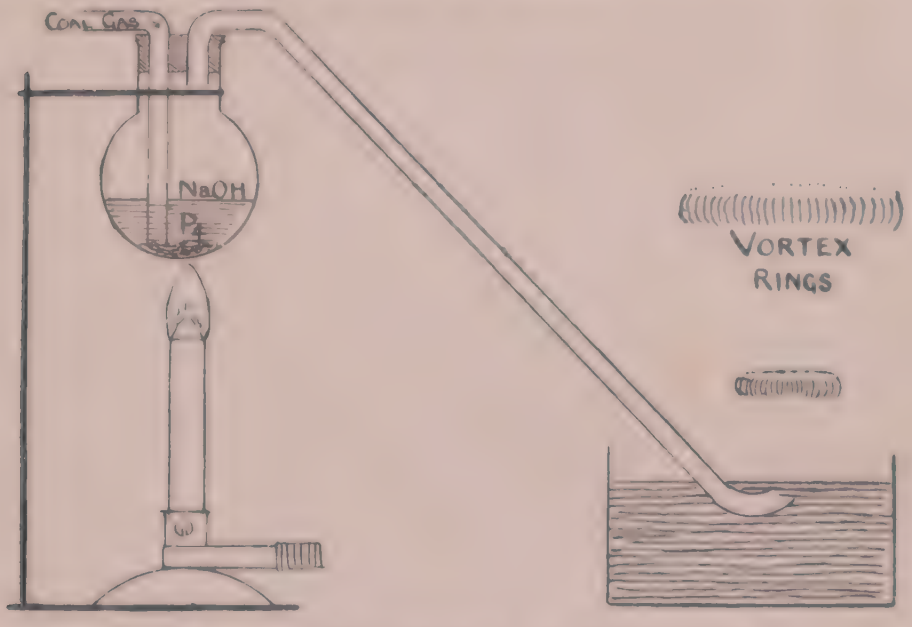


FIG. 11—PRODUCTION OF PHOSPHINE

It is very important that all air be expelled from the flask before heating. This is done by passing in coal gas. When the experiment is completed coal gas should again be passed in until the whole apparatus is cool. If this is not done there is liable to be an explosion. As phosphine is poisonous this experiment should not be continued in the open for any length of time.

Phosphine (PH_3) is produced together with small quantities of P_2H_4. It is this P_2H_4 which takes fire on coming in contact with the air.

$$4P + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3.$$

Thus a substance may spontaneously burn in air.

4. New Theory

Fire is not a substance or element, neither is it the escape of a subtle influence like phlogiston.

Combustion is not limited to certain substances, but is the result of chemical combination or decompositon. When these chemical processes take place at a high rate, and when gases are evolved, we get the phenomenon of fire—that is, the substances possess the property of giving out light as well as heat; but the living of a plant, our own living process, and the rusting of iron are no less combustion.

When substances burn there is no loss of material but merely a change.

The velocity is largely dependent on what is called chemical affinity or the attraction or liking of certain bodies for one another.

5. Summary

1. *History*—Worship of fire. Fire as an element. Only 150 years ago. Burning as escape of phlogiston. Increase in weight led to negative weight of phlogiston.

2. *Early Investigation*—

1. Candle in air—goes out—
   (*a*) Either forms poison, or
   (*b*) Takes essential out of air.
2. Phosphorus in marked tube—$\frac{1}{5}$ goes.

1660. *Boyle* and *Mayow*. *Result* : "Foul air," "fire air."

3. *Second Stage*—Rey has found substances increased in weight.

1. Candle; catch products by lime.
2. Copper weighed and heated.

Results (*a*) Phlogiston has negative weight, or
(*b*) Fire air is taken up on burning.

4. *Search for Fire Air*—Found in three ways: (1) Scheele: heat, KNO_3; (2) Priestley: heat, Pb_3O_4 and HgO; (3) Lavoisier: heat, HgO. Not till 1774 due to phlogiston theory.

5. *Modern Theory*—Combustion is usually combination with oxygen. When this is rapid, get *fire*.

1. Burn in air and in oxygen, sulphur, iron, charcoal, etc.
2. Relative term. Burn *air* in coal gas.
3. Water will not necessarily quench fire. Burn potassium on water.
4. Water may cause fire. Drop water on to Na_2O_2+sugar.
5. Burning under water. Pour strong H_2SO_4 down funnel on to P+$KClO_3$. (This is dangerous.)
6. Burn Dutch metal or antimony in chlorine.

6. *Results*—Burning is chemical combination at high rate. Refer to human combustion.

6. Results

(A) *Ideas*—

1. Chemical combination.
2. Chemical decomposition.
3. Chemical affinity.
4. Velocity of reaction.
5. Slow combustion.

(B) *Substances*—

1. Nitre.
2. Red lead.
3. Sulphur and SO_2.
4. Carbon and CO_2.

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CHAPTER IV

CHALK

1. History

It is difficult to discover the entrance of chalk, marble, and limestone into the service of man. Where the two latter occur they have been used for building purposes from earliest times. In such places as Egypt, where there is no natural outcrop, the making of bricks was early developed; but where this necessity did not arise the natural limestone or marble had been used. India furnishes splendid examples of the early use of marble. Moreover, the ancients seem to have known the secrets of mortar, and thus were probably familiar with the manufacture of lime.

Lime-kilns were used in this country by the Romans, and there are still traces in the Lake District and Derbyshire. The Romans required the lime not only for building purposes but for mining operations. They bored a hole in the ground and filled it with lime, and then poured water down. This generated heat, and expansion took place, with the result that a cavity was formed. The operation was then repeated, and so on, until the iron was reached. On the Furness iron-field there are evidences of this type of mining.

It is interesting to note that the Latin word for lime is " calx," a term which afterwards came to mean " ash."

The first real gravimetric work was done on lime. The phlogistic period was the period of qualitative

chemistry, and whilst certain progress was made there could be no real progress until quantitative work was begun. This did not take place until the close of the phlogistic period, in 1755, when Black used the balance, and determined accurately the loss of weight when limestone is heated and the quantity of "Fixed Air," or carbon dioxide, produced. This beginning of Physical Chemistry was to be the key to all real advance.

2. Decomposition

1. *Gravimetric*—Heat some magnesite ($MgCO_3$) in a crucible after weighing, and weigh on cooling. Note the loss in weight. What has escaped? (Limestone cannot be heated strongly enough in a crucible to cause decomposition.)

2. *Heating Limestone*—Heat some limestone in a fireclay crucible and lead off the gas. Note that it puts out a light and turns lime-water milky. Note also that it dissolves in water and forms an acid.

3. *Production of Lime*—Heat some limestone in a fireclay crucible and produce lime. Show the action of water on lime and the production of slaked lime. Show that lime-water turns red litmus blue, and is the opposite to the other substance produced. Thus limestone consists of two parts:

(1) Carbon dioxide, a gas.
(2) Lime.

$$CaCO_3 \longrightarrow CaO + CO_2.$$

The production of this gas and its deadly effects are seen occasionally in the chalk-mining districts, where tramps, sleeping in chalk quarries, are sometimes found dead.

In Java there is a valley, or deep cañon, known as the "Guevo Upas" or "Poison Valley," owing to the collec-

tion of this deadly gas at the bottom, the rock being chiefly limestone.

Near Naples we have the " Grotto de Cane," or " Dog's Grotto," into which if a man enter he can live, but if a dog enter he dies. This shows the heavy nature of the gas. This gas is also encountered in mines, in limestone districts especially, and is known as " choke damp."

3. Formation of Carbon Dioxide

1. Test the action of acids on lime and chalk. Note that in the case of lime there is no action.

2. Act with hydrochloric acid on marble, and collect the gas by downward displacement. Note its chief properties.

(*a*) It is heavier than air, and can be poured downwards from one vessel to another.

(*b*) Note the effect of the gas on lime-water. The gas was obtained by heating limestone. What is now happening? The opposite process is taking place, and limestone is being formed from the lime in solution.

(*c*) Note that the gas is extremely soluble in water. This is made use of in the manufacture of mineral waters, which are merely carbon dioxide dissolved in water, with sugar and flavouring added. Soda-water is carbon dioxide and water only, and is termed " soda "-water because it is made from a carbonate of sodium instead of calcium.

(*d*) Note that an ordinary taper is extinguished by carbon dioxide. The presence of " choke damp " is detected by its effect on lights.

(*e*) Burn magnesium in carbon dioxide. Note

the black deposit of carbon and the white deposit of magnesia, which latter was noted in the case of burning magnesium in oxygen. What does the magnesium want? It takes out the oxygen and leaves the carbon. Carbon dioxide, then, consists of carbon and oxygen. Thus our limestone consists of lime, carbon, and oxygen.

$$2Mg_2+2CO_2 \longrightarrow {}_4MgO+C_2.$$

4. Natural Processes

1. *Animals and Plants*—The production and absorption of carbon dioxide are continually going on in Nature. It is possible that before the appearance of animals on the earth the atmosphere contained a much higher percentage of carbon dioxide, and that in this atmosphere plants lived and gradually purified it.

Animals and plants largely consist of carbon, as can be proved by the production of carbon on the partial combustion of their remains. Now carbon dioxide is formed when carbon burns, and the process of breathing in man, animals, and plants is one of slow combustion of carbon. Thus, when we breathe out we expel a mixture of nitrogen and carbon dioxide. This is proved by breathing into lime-water. If this were the only process carried on the air would get more concentrated with carbon dioxide.

Plants, however, under the action of sunlight, have the power of decomposing carbon dioxide into carbon monoxide, which they require, and oxygen, which they expel. This can be shown by immersing a plant in water under a bell-jar and exposing it to sunlight. Bubbles of gas arise and collect at the top. On testing it is found that the gas is oxygen.

Or, expose to sunlight some watercress in a bell-jar

or gas receiver full of soda-water. The same thing will happen. Why are trees grown in crowded streets? Not only for beauty and effect, but to reduce the amount of carbon dioxide present in the atmosphere.

2. *Combustion*—Most forms of combustion use up oxygen with the production of carbon dioxide. This is true of fires, stoves, gas-jets, and lamps. Fires produce ventilation, but stoves, lamps, and gas-jets are injurious unless sufficient ventilation is supplied. Hence, crowded and lighted rooms often give rise to headaches.

3. *Germination and Fermentation*—The process of sprouting which results in the decay of the seed case forms carbon dioxide. In fact, wherever decay is going on this gas is being formed.

Allow some seeds to sprout in water under a bell-jar, and note the formation of carbon dioxide.

Fermentation, which is also a process of decay, results in the formation of carbon dioxide. In the manufacture of certain alcoholic beverages, such as beer and champagne, this carbon dioxide is retained, and causes frothing in one case and sparkling in the other.

Allow sugar to ferment by the action of yeast in a flask, and lead off the carbon dioxide.

4. *Natural Waters*—A number of natural waters contain large quantities of carbon dioxide dissolved, and have medicinal properties. Many holy wells were of this type. The waters of Buxton contain very large quantities of this gas. Hence the term "mineral waters" applied to those of artificial manufacture.

It will be seen that Nature is continually producing this gas, not only by the breathing of animals and plants, but by combustion and decay; but that a method of freeing the air from it is also supplied by the action of plants and by the fact that the gas is soluble in water. These natural processes are identical with those worked

in the chemical laboratory, and have been in operation since the beginning of life; but in one case—the action of plants in freeing the air of CO_2 (carbon dioxide)—it is impossible by artificial means to perform Nature's operation.

5. Lime

We next proceed to an examination of the second substance obtained from limestone.

1. *Pour Water on Lime*—Note the heat generated. We produce slaked lime or "milk of lime." Lime is partly soluble in water, and if the clear liquid be drained off we get lime-water.

Slaked lime is used largely in whitewashing processes, and as milk of lime is given as a medicine. It is often necessary as a food in districts where the water is very soft and children are liable to develop rickets. Note that the slaked lime is capable of turning red litmus blue. The production of slaked lime is as shown:

$$CaO + H_2O \longrightarrow Ca(OH)_2.$$

2. *Lime-water* is merely a solution of lime. It is used as a medicine, and, mixed with oil, forms a splendid curative for scalds or burns. It is given in the case of acid poisoning, as it is the opposite of an acid—that is, it is an alkali. Alkalies themselves are very injurious to the human system, but this one is so weak that it has no ill-effects, but is able to destroy the power of the acid or neutralize its effects.

Lime-water also forms about one-half of most lime creams and other substances used for hair, the other half usually being olive oil or some other oil.

3. *Pass Carbon Dioxide into Lime-water*—Note that a milky appearance is produced, and on filtering a chalky deposit is obtained, which, when acted on by acids,

again gives carbon dioxide. This deposit must therefore be limestone or chalk.

$$Ca(OH)_2 + CO_2 \text{ (carbon dioxide)} \longrightarrow CaCO_3 + H_2O.$$

If, however, we continue to pass in carbon dioxide the milky appearance goes, and the water again becomes clear. This is due to the fact that water containing carbon dioxide is able to dissolve chalk. This is proved by heating the now clear liquid and driving off the carbon dioxide. The water again becomes milky, and a white deposit is obtained.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2.$$
$$Ca(HCO_3)_2 \xrightarrow{\text{(heated)}} CaCO_3 + H_2O + CO_2.$$

This process continually goes on in kettles which have to boil hard water. Hard water contains carbon dioxide and so dissolves limestone. When the water is boiled the limestone comes out as "fur" on the sides of the kettle, unless a stone or marble is put in the kettle when it forms there. It is very dangerous to boil such water in the boilers of steam-engines. The "fur" may become very thick, so that the iron of the boiler gets red-hot. Then the fur cracks, and the water comes in contact with the red-hot iron. A tremendous amount of steam is generated, and the boiler bursts. Thus boilers have to be continually cleaned.

4. *Action of Air on Quicklime*—Stand some quicklime in a jar for several days in an atmosphere of carbon dioxide. Then treat the lime with acid and note the effervescence due to the escape of carbon dioxide. The lime has changed to limestone, taking up carbon dioxide.

$$CaO + CO_2 \longrightarrow CaCO_3.$$

This process is continually going on in the hardening of mortar, and, in fact, if it did not mortar would be

useless for cementing stone or brick. Mortar consists of lime and sand, and the lime turns to limestone. There is also an action on the sand due to contact with the lime in the presence of carbon dioxide.

6. Hardness of Water

Water varies in certain districts with regard to the ease with which a lather of soap can be formed. In some districts it is quite easy to wash, but in others a scum forms on the water, and it appears to be "hard." Of all waters rain-water most easily forms a lather. Thus many people collect rain-water for washing clothes, knowing that the hard water uses more soap. Why are some waters "soft" and others "hard"?

1. Test several kinds of water, including distilled water, with a standard soap solution.

2. Pass carbon dioxide into lime-water. It is turned milky because limestone is formed. Continue to pass it in and the milkiness goes. Now test this, and see that it is hard water. Boil, and it becomes milky again. Filter, and see that it is soft water now.

Thus the hardness is due to limestone or chalk being dissolved in the water. By boiling this hardness is removed, because the carbon dioxide is driven off and the limestone is deposited. Thus boiled water washes clothes more easily than cold water. This hardness is called temporary because it can easily be removed.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2.$$

3. This hardness can also be removed by adding lime to the water. This is sometimes done in limestone districts, and thus the water, when drawn from the tap, appears milky.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 3H_2O.$$

4. The presence of too much limestone in water used for drinking purposes may be dangerous, causing the swelling of certain glands in the neck called thyroid glands. In Derbyshire, for instance, people often suffer from "Derbyshire neck." On the other hand, too little limestone in water is also dangerous to children, and is often the cause of a disease called "rickets," which gives rise to bow-legs. Lime is essential to the formation of bones, and where the water is too soft lime-water is often given in children's food.

5. Stand some plaster of Paris in contact with water for several days. Filter, and test the water with soap solution. It is "hard." Boil, and see that it is still "hard." This is called "permanent" hardness, because it cannot be got rid of by boiling.

Now add some washing soda to the solution, and test again. It is now "soft."

$$CaSO_4 + Na_2CO_3 \longrightarrow$$

$CaCO_3$ (calcium carbonate or limestone) + Na_2SO_4.
(Solid comes down.)

6. Add some magnesium chloride to some water and test with soap solution. It is "hard." Boil, and note it is still "hard." Add some washing soda and it is now "soft."

$$MgCl_2 + Na_2CO_3 \longrightarrow MgCO_3 + 2NaCl.$$
(Solid comes down.)

This also is "permanent" hardness.

7. Test some sea-water. It is very "hard," and boiling does not soften it. This sea-water contains a fair quantity of magnesium chloride and other salts. Special "marine soap" has to be used at sea. This contains a softener other than washing soda, for washing soda is injurious to the skin. Ammonium and potassium carbonates act well as softeners. Dry soaps used in washing clothes usually contain anhydrous sodium carbonate.

8. Why does soap not form a lather with hard waters?

Soap consists of sodium stearate (not all soaps), and is soluble in water. But if $CaCO_3$ (calcium carbonate) is present, calcium stearate is formed, which is insoluble in water, and forms as a scum on the water. The same happens with a magnesium salt, magnesium stearate being formed. Thus sufficient soap must be used to use up all the calcium and magnesium salts before a lather can be formed.

$$\underset{\text{(soap)}}{2NaC_{18}H_{35}O_2} + CaCO_3 \longrightarrow \underset{\text{(calcium stearate)}}{Ca(C_{18}H_{35}O_2)_2} + Na_2CO_3.$$

$$2NaC_{18}H_{35}O_2 + MgCl_2 \longrightarrow \underset{\text{(magnesium stearate)}}{Mg(C_{18}H_{35}O_2)_2} + 2NaCl.$$

9. Thus there are two kinds of hardness in water—

(*a*) Temporary—removed by boiling or by adding lime.

(*b*) Permanent—removed by adding sodium carbonate.

All hardness is removed by distilling water.

How do these salts, causing hardness, get into the water? By the water sinking into the ground and dissolving them.

7. Summary

1. *History*—Marble building. Formation of lime in kilns—use in mining operations by Romans by pouring water on lime (show this). First use of balance made by Black, 1755. Heated chalk.

2. *Decomposition*—

1. Heat, after weighing.
2. Heat, and show action on lime-water.
3. Heat, and produce lime. Action of water on lime. Action on litmus.

Thus two substances—lime and "fixed air."

Refer to deaths in chalk-pits from CO_2; also "Guevo Upas," or Poison Valley of Java. "Grotto de Cane," or Dog's Grotto at Naples. (Dog suffocated—man can live. Why ?)

3. *Formation of* CO_2

1. Action of acids on lime and chalk.
2. HCl on marble. Collect.

Properties: (*a*) Heavy nature.
(*b*) Effect on burning.
(*c*) Effect on lime-water—*cf.* breathing.
(*d*) Solubility in water. Mineral waters.
(*e*) Burn magnesium in CO_2 and get carbon.

4. *Natural Processes*—

1. Animals and plants—germination and production of CO_2.
2. Fermentation.
3. Natural waters.
4. Action of plants in sunlight. Watercress in soda-water.

5. *Lime*—

1. Slaked lime—calcium hydrate.
2. Lime-water.
3. Pass in CO_2. Filter, and add acid.
4. Stand quicklime in jar of CO_2 for day. Then add acid. Mortar.

6. *Hardness of Water*—Chalky districts. Washing. *Cf.* rain-water.

1. Pass CO_2 into lime-water; milky, then clear boil.

2. Act with soap solution, formation of scum.
   Temporary Hardness—Boiling.
   Permanent Hardness—Use of washing soda.
   Sea-water Hardness—Marine soap (washing soda).

8. Results

(A) *Ideas*—

1. Direct decomposition by heating.
2. Alkali and acid.
3. Respiration, germination, fermentation.
4. Temporary and permanent hardness of water.

(B) *Substances*—

1. Limestone.
2. Lime.
3. Lime-water.
4. Calcium sulphate.
5. Magnesium chloride.

CHAPTER V

COMMON SALT

1. History

Salt has been known from earliest times because it occurs naturally in the sea and in the form of rock-salt. Its properties of preserving were known and used by the Jews and other ancient peoples. Biblical references to salt are numerous. The question of "Why is the sea salt?" has long agitated the minds of men, and has given rise to many fairy stories, such as that of the "salt-grinder."

Salt was mined in Cheshire by the Romans by means of brine springs, and the famous Wielicza beds were being mined A.D. 1000; but its examination was long delayed. Probably the first to produce chlorine was Stephen Hales 1677-1761), a parson of Teddington. The first authentic discovery was that of Scheele's in 1771-1774. He discovered the gas by the action of hydrochloric acid on pyrolusite (manganese dioxide), and regarded it as muriatic acid deprived of oxygen. In 1785 Berthollet examined the gas, and came to the conclusion that it was muriatic acid + oxygen. For long it was thought to be an oxide of muriatic acid (HCl). It was Davy, in 1809, who first settled that this green gas was an element. He, indeed, made a very thorough examination of its properties.

2. Occurrence

1. Salt occurs in this country in Cheshire, at Middlewich, Nantwich and Northwich; in Worcestershire, at Droitwich; and at Walney Island, near Barrow-in-Furness.

In Cheshire it is both mined and brought to the surface as brine. Sometimes brine springs occur naturally, and in other cases a boring is made and water put down and then the brine pumped up. The ravages played by this mining can be seen in Middlewich, where houses sometimes slope at 30 degrees to the vertical.

The beds in Cheshire are from 75 feet to 150 feet thick, and occur in about seven veins.

These mines have worked continuously since 1670.

2. At Wielicza, in Galicia, are the most wonderful salt-mines in the world. Here the beds are about 1,200 feet thick, and occur in about thirteen veins. Whole families live down the mines, and ponies are perpetually stabled there.

3. Salt is also produced at Staussfurt in Germany, Russia, Spain, and the United States.

The United States is the largest salt-producing country in the world, producing three million tons per year, and we come next with two million tons.

4. A large amount of salt is obtained from the sea and inland seas. This industry is carried on largely around Marseilles, in Sicily, along the northern shore of Spain, and at Salt Lake City in Utah.

5. *Methods of Preparation*—There are four processes for preparing salt.

(A) *Pan Process*—The first is the normal process used with brine obtained by mining. The solution of rock-salt is boiled in riveted pans. There are three types of pans, producing three types of salt.

(1) *Small Pans*—In the small pans the temperature is kept at about 107° C., and the operation takes from eight to twelve hours. A perforated spade, called a "skimmer," is used for removing the salt. The crystals produced are small, and suitable for use as table salt.

The salt is then dried by rotating in copper cylinders.

It is most important that salt should be dry, and kept dry, as moist salt under the action of sunlight forms a poison named hypochlorous acid (HClO). Thus, "If the salt have lost its savour wherewith shall it be salted."

Cerebos salt contains calcium phosphate, which tends to prevent it becoming damp.

(2) *Intermediate Pans*—Here the temperature is kept at 60° to 80° C., and the operation takes from twenty-four to forty-eight hours. A coarser grain salt is produced.

(3) *Large Pans*—The temperature is kept at 38° to 60° C., and they are usually cleared monthly. The salt produced is usually impure, and known as "bay-salt" or "hoppers," sometimes as "fishery salt," because it is used in curing fish. The addition of alum increases the size of the grains, whereas glue or grease will reduce them.

In all cases there are certain deposits in the pans, which have to be cleaned periodically. The chief are:

(*a*) Sand scale ($CaCO_3$).
(*b*) Pan scale ($CaSO_4$).

(B) *Multiple Evaporators*—A sytem of evaporation under reduced pressure was invented in 1839 by Reynolds, and set up in Germany. The system is also now set up in this country. It is usual to have a triple system, and not only is the operation carried out much more quickly, but there is economy in fuel and labour.

(C) *Solar Salt*—The Atlantic contains 3 per cent. of salt; so does the Mediterranean; the Dead Sea contains 8 per cent., and the Great Salt Lake 20 per cent.

The chief works in Europe are at the mouth of the Rhone. The brine is run into large reservoirs, and allowed to be evaporated by the sun. During the process it is raked, or "puddled," and, being thus mixed with

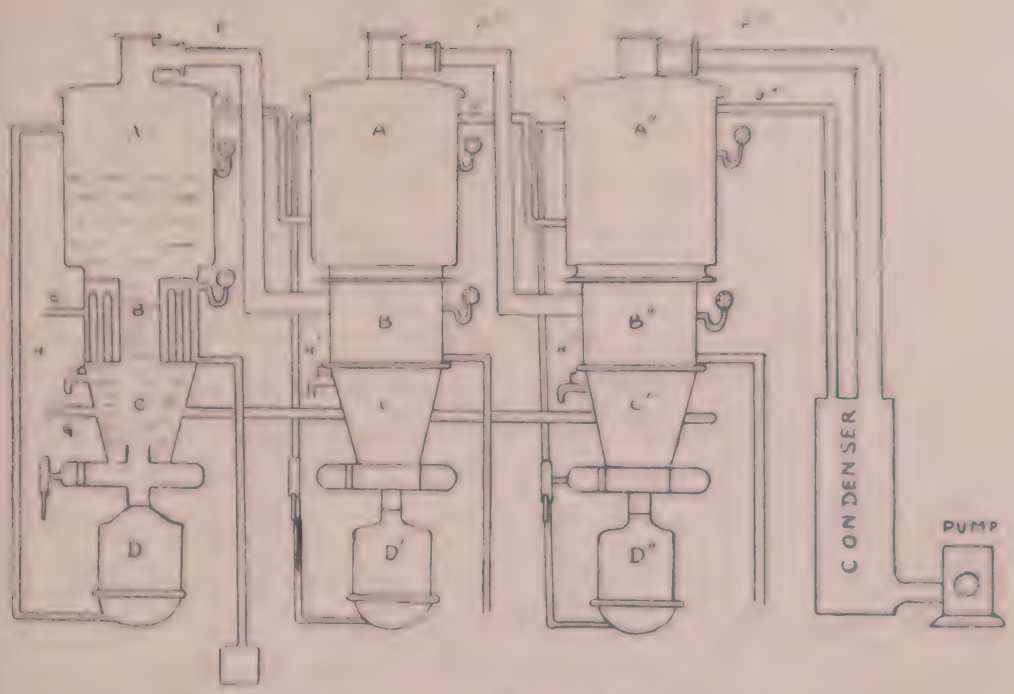


FIG. 12—MULTIPLE-EFFECT EVAPORATORS

Salt solution enters the boiler A. Its boiling-point is lowered by diminution of pressure caused by the pump, and it is heated by a bundle of steampipes in B. The steam is generated in the boiler and passes out at E. Evaporation takes place in A. The steam escaping is below 100° C., and, passing through F, reaches B′, and heats the liquid in A′ where the pressure is still lower. So the liquid in A′ boils. The vapour from the last boiler is condensed in the condenser, thus further lowering the pressure. The solution enters the boilers through G, and as salt crystallizes it passes into D, which has a perforated false bottom and retains the salt. The mother-liquor returns to the boiler by H. Every two or three hours salt is discharged. One ton is made every twenty-four hours by a triple evaporation.

The brine must be first purified by slaked lime and ammonium carbonate, or gypsum will choke the pipes.

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$
$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + H_2O$$
$$(NH_4)_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2NH_4Cl$$
$$(NH_4)_2CO_3 + CaSO_4 \rightarrow CaCO_3 + (NH_4)_2SO_4$$

clay, a larger surface is exposed, and so evaporation takes place more quickly.

(D) *Fusion, or Lee's Process*—This was first tried in Ireland, in 1903. At 815° C. rock-salt melts, and the pure salt can be run off. This salt before the war could be produced at the cost of 2s. 6d. per ton.

3. Examination

1. Heat salt. It does not melt, but fuses.
2. Heat some in a flame on platinum wire, and note the yellow colour given to the flame. This yellow colour is peculiar to the metal sodium.

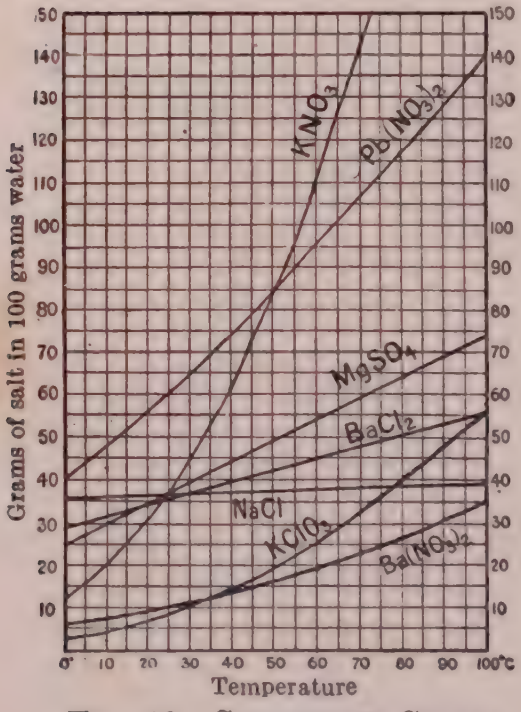


FIG. 13—SOLUBILITY CURVE SHOWING COMMON SALT

3. Dissolve some salt in water and form brine. Heat, and show that hot water dissolves very little more than cold water.

4. Evaporate the solution and get the salt back.

Brine is used for curing bacon, fish, etc. A solution of salt, usually called saline, is used as an antiseptic in the treatment of wounds, and is also pumped into the veins to keep up the blood-pressure and maintain the action of the heart in cases of loss of blood.

4. Reactions

1. Act on salt with strong sulphuric acid. Note the effervescence. A gas is given off. Test this gas with litmus paper and see that it is an acid.

Perform the operation in an evaporating dish, and evaporate the liquid. Note that the white solid left is not common salt. Taste it.

2. Collect the gas given off as shown.

$$H_2SO_4 + 2NaCl \longrightarrow Na_2SO_4 + 2HCl.$$

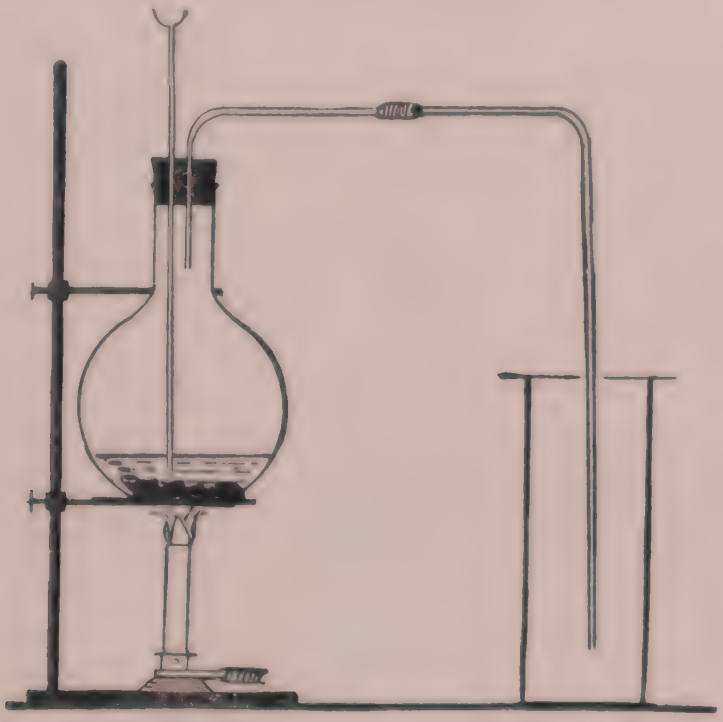


FIG. 14—COLLECTING HYDROCHLORIC ACID GAS

Collect several jars, and note its properties.

(*a*) Does not burn.
(*b*) Puts a taper out.
(*c*) Slightly heavier than air.
(*d*) Readily soluble in water.
(*e*) Acid.
(*f*) When brought near ammonia it forms dense white clouds.

3. Show the great solubility of HCl (hydrochloric acid) by a fountain as shown.

Fill the flask with dry HCl (hydrochloric acid) gas, and connect by means of the rubber tube and clip to the bottle of water. Remove the clip, and blow gently at *A*. This causes water to enter the long tube and dissolve

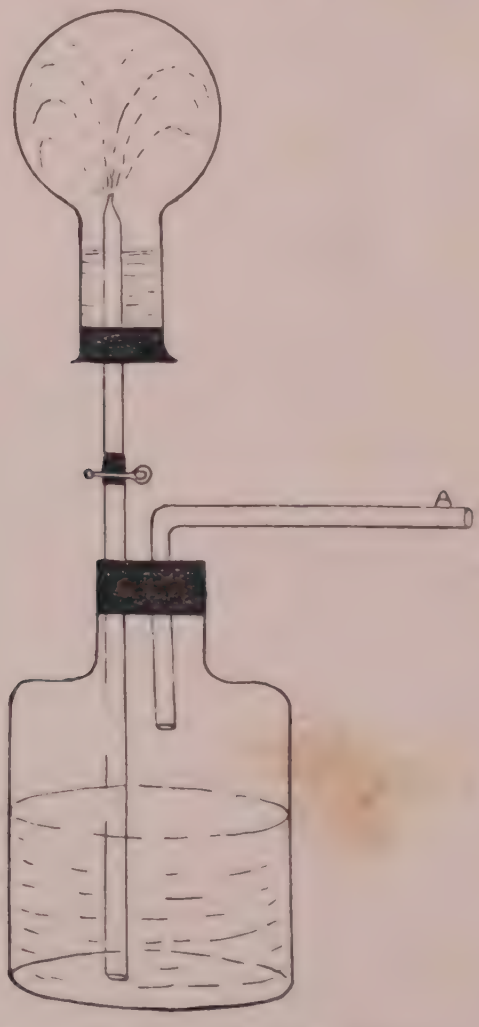


FIG. 15—HYDROCHLORIC ACID FOUNTAIN

the HCl (hydrochloric acid) present. The vacuum created causes the water to rush up the tube and form a fountain in the flask.

If the water is coloured with blue litmus it will be turned red.

Water dissolves 505 times its own volume of HCl (hydrochloric acid) at normal temperature and pressure.

4. Prepare in a dark room some bulbs containing equal quantities of hydrogen and chlorine. Expose these to sunlight. They explode.

Note a red light does not cause the gases to explode. Test various lights by coloured glasses.

4. Explode H (hydrogen) and Cl (chlorine) in equal volumes in a eudiometer by means of an electric spark. Note there is no diminution of volume, and that the residue is an acid, to all intents and purposes the same acid produced when strong sulphuric acid acts on common salt. Salt, then, seems to contain chlorine.

The following table shows that the rate of explosion of H (hydrogen) and Cl (chlorine) is considerably affected by the introduction of a foreign gas.

Foreign Gas	*Volume of* $Cl_2 + H_2$	*Volume of Foreign Gas*	*Rate of Combustion*
None	1,000	0	100
HCl	1,000	1·3	100
Cl_2	1,000	10	60·2
Cl_2	1,000	75	50·3
Cl_2	1,000	180	41·3
H_2	1,000	3	57·8
O_2	1,000	5	9·7
O_2	1,000	13	2·7

5. Chlorine

1. Electrolyze a solution of common salt. This can be carried out by using carbon electrodes, as the chlorine coming off attacks the metal electrode. The operation must be allowed to proceed for some time, as carbon absorbs chlorine. The result should be sodium at one pole and chlorine at the other; but the sodium is never freed but is given up as sodium hydrate, so only chlorine

is collected, and the solution gradually becomes alkaline. Test the chlorine by smell.

If fused salt is electrolyzed, then sodium comes off at one pole and chlorine at the other. This is a commercial process in the production of sodium.

Thus salt is a compound of sodium and chlorine.

2. Prepare chlorine by the action of hydrochloric acid on manganese dioxide. The hydrogen of the hydrochloric acid is taken up by the oxygen of the manganese dioxide, and the chlorine is given off.

$$4HCl + MnO_2 \longrightarrow 2H_2O + MnCl_2 + Cl_2.$$

This is prepared in the same way as HCl (hydrochloric acid) gas in the previous experiment.

3. Prepare chlorine from common salt by H_2SO_4 (sulphuric acid) and MnO_2 (manganese dioxide). It is better to fuse the salt first to get good results.

$$2NaCl + MnO_2 + 2H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

This is prepared as in Experiment 2.

4. Examine the properties of chlorine.

(1) Heavier than air.

(2) Pungent odour. Refer to poison gas. Chlorine suitable because (*a*) heavier than air; (*b*) easily liquefied; (*c*) cheaply produced.

(3) Greenish colour, but white when in the form of a cloud.

(4) Does not burn in air.

(5) Burns in hydrogen, forming HCl (hydrochloric acid). This is performed in the same way as air was burnt in hydrogen.

(6) Does not readily support combustion, but many things will burn in it.

(*a*) A strongly burning taper will burn, forming a large deposit of carbon. A taper

is composed largely of carbon and hydrogen, so the carbon is set free and hydrochloric acid is formed.

(*b*) Hydrogen burns readily in a jar of chlorine, forming hydrochloric acid.

(*c*) Sodium, if first melted in a deflagrating spoon, can without danger be plunged into a jar of chlorine, and will burn, forming common salt. The salt can be tasted. This proves that common salt is a compound of sodium and chlorine.

(*d*) Finely powdered antimony or bismuth, if gently heated first, burns spontaneously in chlorine.

(*e*) Dutch metal (copper leaf) and gold leaf both burst into flame when plunged into a jar of chlorine.

(*f*) A filter paper dipped in turpentine burns spontaneously on being plunged into chlorine, forming a thick deposit of carbon.

5. *Absorption of Chlorine by Charcoal*—Refer to the box respirator, and, if possible, take one to pieces. Inside is a mixture of charcoal and soda-lime soaked in permanganate of potash. At first we relied on the chemical principle to destroy the effects of chlorine, but later only on the absorption principle. Pass some chlorine through a bulb of charcoal and show that it is absorbed. Charcoal has the property also of removing colour. Take a beaker containing a solution of potassium permanganate. Add charcoal, and filter. The filtrate is colourless. Thus charcoal is used in refining sugar. Its property of absorbing gases causes it to be used in drains.

Heat the charcoal, which contains chlorine, and show that the gas is given off. The problem of where the gas

goes, and in what state it is contained, is still a mystery. The carbon appears to grow no larger, and is only heavier.

The following table shows the relative properties of alcohol, water, and charcoal in absorbing gases. It will be seen that, with the exception of ammonia and hydrochloric acid, charcoal leads the way.

Gas	1 *Volume* H_2O	1 *Volume Alcohol*	1 *Volume Charcoal*
NH_3	1,127	—	171
HCl	505	—	170
H_2S	80	17·9	110
SO_2	4·4	—	130
C_2N_2	2·5	—	107
CO_2	1·8	4·3	67
N_2O	1·3	—	85
C_2H_4	·25	—	75
Cl	—	—	73
NO	—	—	70
CO	—	—	21
O_2	·04	·28	17
A	·04	—	—
N_2	·02	·13	15
H_2	·01	·07	4

The following table shows the increase of absorption, with decrease in temperature, for charcoal. Thus, in hot weather the box respirator was less efficient than in cold weather.

Gas	*Volume Absorbed* 0° *C.*	*Volume Absorbed* −185° *C.*	*Heat Evolved* (*Calories*)
H_2	4	135	9·3
N_2	15	155	25·5
O_2	18	230	34
A	12	175	25
Hc	2	15	2
$2H_2 + O_2$	12	150	17
$2CO + O_2$	30	195	34·5
CO	21	190	27·5

6. *Bleaching Properties*—Make a solution of chlorine in water. Allow several coloured objects to stand in it, including flowers. Note that they lose their colour. This is probably due to the production of oxygen in what is termed a nascent state. The oxygen bleaches by oxidizing the colouring matter.

$$H_2O + Cl_2 \longrightarrow 2HCl + O.$$

Thus, in bleaching with chlorine we get hydrochloric acid formed, and this is harmful to the fabric being bleached.

Bleaching powder is made by passing chlorine into slaked lime. The lime is raked during the process. What really happens is not known. It has been supposed that the lime merely acts as a carrier of chlorine, but it is more likely that the hypochlorite of lime is formed—

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O.$$

The hypochlorite breaks down in the presence of carbon dioxide, giving chlorine,

$$Ca(OCl)_2 + CO_2 \longrightarrow CaCO_3 + Cl_2,$$

and the chlorine bleaches as before. In the presence of mineral acids the same takes place.

Hypochlorous acid itself when present is very unstable, and readily breaks down.

$$2HClO \longrightarrow 2HCl + O_2.$$

6. Summary

1. *History and Occurrence*—Very old. Preservative. Biblical allusions. Mines of Cheshire. Austria. Evaporation of sea-water in Spain and France. Two million tons produced in this country. Used in glazing and for making washing soda.

2. *Examination*—

1. Heat—does not melt, but fuses.
2. Heat in flame on platinum wire—yellow.
3. Solubility—not increased on heating. Brine.
4. Evaporate and get salt back. Taste.

3. *Reactions*—

1. Action of strong H_2SO_4. Test gas with litmus paper. Solid left is not salt.
2. Collection of gas (HCl).

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl.$$

Properties: light put out; solubility (HCl *fountain*). Action on metals.

3. Explosion of H and Cl under sunlight.

4. *Chlorine*—

1. Prepared from salt.

$$2NaCl + MnO + 2H_2SO_4 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

2. Electrolyze solution of salt (commercial).
3. Properties: refer to poison gas. Absorbed by carbon (weigh and heat). Burn in Cl: (1) Hydrogen; (2) sodium; (3) antimony; (4) gold; (5) Cu (heat). Show that H gives HCl and Na gives salt. Pour Cl out.
4. Solution in water. Bleaching. Bleaching powder.

7. Results

(A) *Ideas*—

1. Action of acid on a salt.
2. Acid as a gas.
3. Chemical activity of light rays.

4. Coloured gases.
5. Absorption of gases.
6. Bleaching action.

(B) *Substances*—

1. NaCl.
2. Cl.
3. HCl.
4. Bleaching powder.
5. H_2SO_4.

CHAPTER VI

METALS

1. History

METALS have been used by man from prehistoric times. After the Stone Age came the Bronze Age, when man began to make his household utensils and weapons of warfare from metallic substances such as bronze and brass. During this age there are also traces of the use of gold. Bronze and brass are not pure metals, but a combination of two metals. Pure metals, such as copper and lead, came to be used much later because they usually occur in their ores in combination with some other metals. Hence the early use of such alloys as bronze and brass. But to use even these, prehistoric man must have understood the art of smelting. Iron was used much earlier than either copper or lead because it occurs singly in its common ores.

The silver mines of Nubia were being worked under Rameses II. during the days of Joseph, and it is probable that they were working when Abraham first went down to Egypt. The ancients believed that metals were formed by the penetration of air into the vitals of the earth, so that the further they mined the more metal was produced, and the richer became the vein. It is interesting to note that their work never produced any contradiction of this theory, so they had no reason to reject it. Those were not the days when mines gave out and shareholders became bankrupt.

It is most probable that the Jews learnt the art of

smelting from the Egyptians during their slavery. It is certain that they were very efficient in the work of smelting iron, brass, silver, and gold, and the description of the Tabernacle bears witness to their remarkable ability. Later, the Temple, with still finer workmanship, was erected. A large part of their gold was obtained from India, where mining was early developed.

Tin was mined in Cornwall as early as 300 B.C., and a vigorous trade carried on with the Phœnicians.

The Romans found the Britons with a bronze coinage and using bronze weapons, but iron was practically unworked. The Romans commenced the mining of iron ore in the Furness district and built charcoal furnaces. Some of their furnaces remain to-day, and a few years ago one was actually being worked.

When gold became generally known, and its value appreciated, the alchemists busied themselves in a vain search for the philosopher's stone, not realizing that if it were discovered gold would no longer be so valuable. This search for the philosopher's stone was not only bound up in the transmutation of metals, but in the production of the elixir of life. The persistency of this doctrine through the Dark Ages until quite recent times will be seen from the following quotations:

Suidas (a Greek of the eleventh century): "Chemistry is the artificial preparation of silver and gold."

Paracelsus (1527): "Chemistry is the art of rendering bodies."

Lachaire (1580): "Chemistry is that part of natural philosophy which teaches the preparation of metals on the earth by imitating the operations of Nature in the earth as closely as possible."

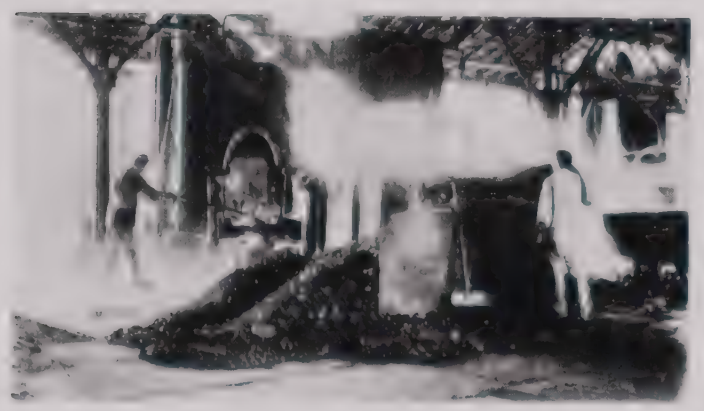
Salmon (1672): "Chemistry is an art or practical science which teaches the methods of resolving compound bodies into their natural principles, and by this

means rendering them most pure and efficacious as a medicine, either for curing diseases or for perfecting the imperfect metals."

The language used by some of these alchemists in describing their experiments is well exemplified in the following passage from Glauber (1604-1668), in which he describes the "concentrating and amending metals by niter":

"First a man is to be made of iron having two noses on his head, and on his crown a mouth which may be opened and again close shut. This, if it is to be used for the concentration of metals, is to be inserted in another man made of iron or stone, that the inward head only may come forth out of the outward man, but the rest of his body or belly may remain hidden in the belly of the exterior man. And to each nose of the head glass receivers are to be applied to receive the vapours ascending from the hot stomach. When you use this man you must render him bloody with fire to make him hungry and greedy of food. When he grows extremely hungry he is to be fed with a white swan. When the food shall be given to this iron man an admirable water will ascend from his fiery stomach into his head, and thence by his two noses flow into the appointed receivers; a water, I say, which will be a true efficacious aqua vitæ; for the iron man consumeth the whole swan by digesting it, and changeth it into a most excellent and profitable food for the king and queen, by which they are corroborated, augmented, and grow. But before the swan yieldeth up her spirit she singeth her swan-like songs which, being ended, her breath expireth with a strong wind and leaveth her roasted body for meat for the king, but her anima or spirit she consecrateth to the gods, that thence may be made a salamander, a wholesome medicament for men and women."

STEAM HAMMER



PUDDLING

2. Properties

Several metals, including mercury, should be examined. It should be noted that, as far as physical characteristics go, there is no ideal metal, and the distinction between metal and non-metal is sometimes very slight. However, there are certain definite characteristics which are common to the class, such as:

1. They are usually solid. Mercury is an exception.
2. They have a peculiar lustre. This is sometimes true of non-metals, such as iodine.
3. They are usually malleable—*i.e.*, can be beaten into sheets: hence their usefulness.
4. They are usually ductile—*i.e.*, can be drawn out into wires. This, again, makes them most useful.

   It must be remembered that in many cases the introduction of a very small quantity of impurity will destroy these last two properties and make the metal brittle like most non-metals.
5. They are usually elastic: hence their use in making springs, etc.

The ideal metal, from the purely physical point of view, would be perfect in these properties, and is only approached in most of them by gold and platinum, although in some respects these are surpassed by such a substance as steel.

The real distinction is not physical but chemical, and will be referred to later; but even here there are some metals which are very near the border-line, and indeed which, under certain conditions, act as non-metals.

From the chemical point of view the most real metals are those which from the physical point of view would

scarcely be recognized—namely, potassium, sodium, and the hypothetical one, ammonium.

Metals, with the exception of the best physical ones, and therefore the lowest in the chemical scale, like gold and platinum, are rarely found pure, because of their chemical activity. They are mostly fond of oxygen or some other element, and are thus found in ores. It may be that there are huge stores of elemental substances, including metals, at the centre of the earth, forming a store of energy due to chemical separation, and this primeval source of energy may have something to do with the earth's revolution; but this is mere conjecture.

Examination of Chemical Properties—1. Burn several metals in oxygen. Refer to the lesson on Burning, and the formation of calces. Note the increase of weight of copper burnt in air. Examine the residue when sodium, potassium, and magnesium are burnt. The calx dissolves in water, and the solution turns red litmus blue. Such substances are termed alkalies, and are the opposite of acids. Thus the oxides of metals are alkaline in character, whilst the oxides of non-metals are acid. This is the broad chemical distinction. It is only such metals as sodium, potassium, calcium, magnesium, etc., which show this property strongly, and indeed there are some metals, as zinc, which can form acids.

Note the burning of iron and the formation of the black oxide, Fe_3O_4. Refer to the burning of the poker.

When iron rusts a different oxide is formed Fe_2O_3, but the process is slow combustion.

2. Burn some metals in chlorine, including sodium, bismuth, antimony, copper. Note that the residues (especially in the case of sodium) are neither acid nor alkaline. These substances are known as "salts," and these special salts are chlorides.

The ores of metals are usually oxides or salts.

3. Action of Acids

1. Act with hydrochloric acid on various metals and produce salts. It is better to use HCl (hydrochloric acid) as the action is normal, whereas in the case of nitric and sulphuric acids, which are powerful oxidizing agents, the normal reactions rarely take place, and the reaction varies according to the strength of the acid and the heat conditions. In the case of zinc, collect the gas given off, and show that it is hydrogen.

Metals are able to replace the hydrogen in acids and form salts. Evaporate, and examine the salts left.

$$Zn_2 + 4HCl \longrightarrow 2ZnCl_2 + H_2.$$

Some of these salts are soluble and some insoluble in water. The chlorides and nitrates are mostly soluble, but many of the sulphates are insoluble. Many of these salts form the common ores of metals.

4. Common Ores and Metals

(A) Iron—

Ores—The chief ores of iron are:

(*a*) Red hæmatite (Fe_2O_3), which occurs in large quantities in the Furness district, Cleator Moor (Cumberland), and in British Columbia. This is the finest iron ore produced—the best being found in the Furness district; but the cost of mining is so great that some of these iron-fields have at times closed down, owing to the production of less profitable but more easily worked ores. Hæmatite may contain up to 70 per cent. of iron. In many cases it occurs in the form of crystals like long pencils, these combining sometimes to form "kidneys." Pencils are sometimes as long as 6 inches. "Kidneys" in Furness and Cumberland form the staple fireside ornament of miners' cottages. Hæmatite is usually red in

character—a peculiar redness with a kind of sheen; and certain parts of the ore are used for the manufacture of red paint.

The ore often occurs in conjunction with carboniferous limestone, felspar, and quartz. The mines in some cases are 400 yards deep. Blasting is essential, but can be performed with safety and naked lights used, as there are no explosive gases.

(*b*) Brown hæmatite ($Fe_2O_32Fe(OH)_3$). This contains about 57 per cent. of iron, and is found in the Cleveland district, and usually mined in the same way as the red hæmatite.

(*c*) Magnetite (Fe_3O_4). This ore is very rare, and contains about 73 per cent. iron. It is often found in meteors, and possesses magnetic properties. It was probably first found near Magnesia in Asia Minor—hence its name. In early days it was called the Lodestone (leading-stone), and was used to guide ships. It is now worked in Lapland, Sweden, and Siberia.

(*d*) Spathic ore or ironstone ($FeCO_3$). This ore may contain 41 per cent. of iron. It is brown in colour, and often occurs near the surface. It is worked on the oolitic bed, stretching from Oxfordshire in a north-east direction to Lincolnshire, and includes the industries at Wellingborough and Kettering, in Northamptonshire, and Boston and Grantham in Lincolnshire.

It was the opening up of the Northamptonshire beds some twenty-five years ago that caused a serious competition to the hæmatite industry. Very often a field under agriculture is taken over by a mining company. The top layer of grass is cut and laid aside, and then American diggers are brought along to scoop up the ironstone. Light railways connect to the furnaces, and there is a minimum of labour. When all the ironstone has been taken up, the grass is replaced, and the field once more

reverts to pasture or cultivated land. The ironstone is sometimes as thick as 20 feet.

(*e*) Limonite ($2Fe_2O_3 3H_2O$). This ore is a dirty brown in colour, sometimes blue, and contains up to 57 per cent. of iron. It is found chiefly in Spain, around Bilbao, and in South Wales.

"*Pig*" *Iron*—The first process in the manufacture of "pig" iron, with all ores except red hæmatite, is to *calcine* the ore. This is done by stacking with coal and passing in air to regulate the temperature. Shallow kilns are used, and the process helps in the following ways:

(*a*) Most moisture, carbon dioxide, sulphur, and arsenic are expelled. Sulphur and arsenic, even in minute quantities, are detrimental to the manufacture of wrought iron or steel, as they cause brittleness.

(*b*) The ferrous oxides present are changed to ferric oxides.

(*c*) The ore becomes more porous.

The second process is to put the ore into a blast furnace. These furnaces are sometimes 80 feet high, and are now usually served by mechanical power, though some are still filled by hand. The furnace is filled with four parts ironstone, one part of limestone, and two parts of coke, although these quantities vary according to the district. In some cases sand is added to form a flux. Once the furnace is lit it works continuously. The blast is supplied by an engine, and the hot gases given off are used for this purpose.

The changes taking place in the furnace are probably as follows:

(1) $2C + O_2 \longrightarrow 2CO$.

(2) $Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$.

$FeO + CO \longrightarrow Fe + CO_2$.

Thus iron and free CO_2 are formed.

(3) $2Fe+3CO_2 \longrightarrow Fe_2O_3+3CO$.

(4) $Fe_2+3CO \longrightarrow Fe_2O_3+3C$.

This all takes place in the top part of the furnace where the temperature varies from 600° C. to 900° C.

In this part also the following operations are effected:

(5) $CaCO_3 \longrightarrow CaO+CO_2$.

(6) $CO_2+C \longrightarrow 2CO$.

At a slightly higher temperature in the middle of the furnace the reverse of No. 6 takes place:

(7) $2CO \longrightarrow CO_2+C$.

We now get Fe_2O_3 in contact with free carbon at a temperature varying from 1,000° C. to 1,200 ° C., and the final operation takes place:

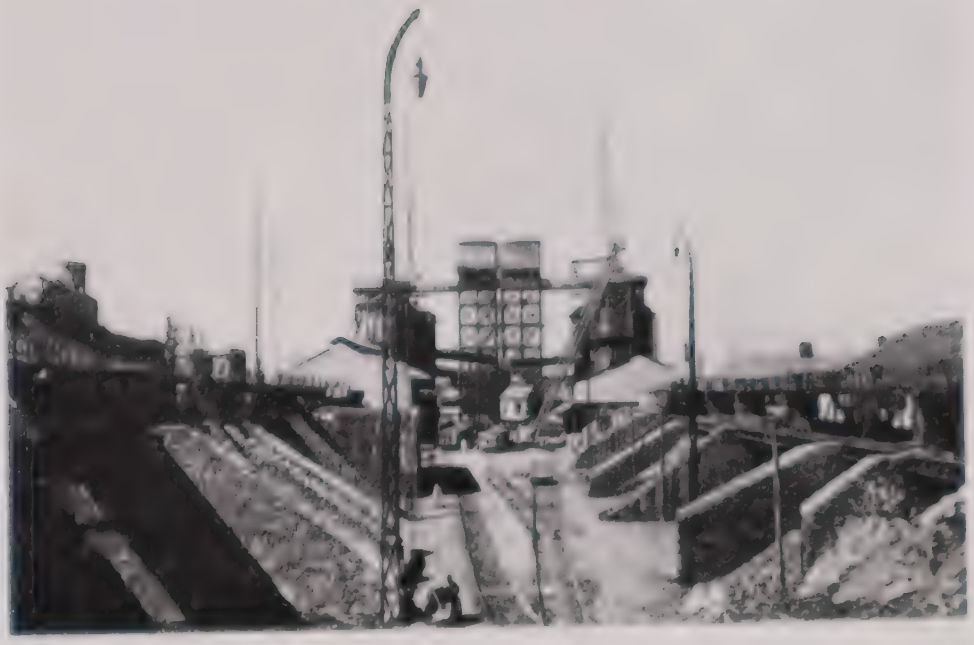
(8) $Fe_2O_3+3C \longrightarrow 2Fe+3CO$.

The whole mass is now spongy, and passes down the furnace, where the temperature increases to 2,000° C. Here it melts, and takes up carbon. In some cases this carbon is contained in solution, and in others in definite combination, probably in the form of carbonyls, such as $Fe(CO)_5$.

The molten metal is run off about every eight hours into sand moulds known as " sow " and " pigs." The slag containing the impurities is run off above. There are two kinds of " pigs."

(*a*) White pigs, containing 3 per cent. carbon in combination. These are produced at a lower temperature, and if treated with acid no carbon remains.

(*b*) Grey pigs, containing 3 per cent. carbon not in combination. On cooling, graphite forms on the outside, and if treated with acid carbon remains.



A BLAST FURNACE

"Pig" iron is brittle and practically useless as a metal.

Wrought-Iron—This contains only 0·5 per cent. of carbon in combination. It is made by heating together in a reverberatory furnace a mixture of ferric oxide and pig iron. Air is sent in whilst the process is going on, the whole mixture is raked, or "puddled," and finally "hammered" by steam-hammers to get rid of the slag. It is then rolled into sheets whilst still hot.

Steel—Steel contains from 0·15 per cent. to 1·15 per cent. of carbon, and so can be made in three ways.

(*a*) *Cementation Process*—This consists of heating together wrought-iron and carbon. The process takes two weeks, and then "blister steel" is produced. This is melted again in graphite crucibles, and a very fine steel produced. This steel is very expensive to make, and is therefore used only for the manufacture of the finest tools and instruments.

(*b*) *Bessemer Process*—This consists in taking cast-iron and heating it in a current of air. The whole mixture is placed in a container which holds ten tons, and the process takes from fifteen to twenty-five minutes. Cast-iron is brought in a molten condition from the blast furnace, and in some cases is carried by electro magnets. When the steel is run out it is cooled in special pits. Otherwise it is necessary to reheat it. After it has cooled some time, it is hammered by steam-hammers, and then rolled into rails or sheets, or made up into "tyres" for railway carriages.

(*c*) *Siemens-Martin Process*—This consists of taking cast-iron and wrought-iron and heating them together in a reverberatory furnace.

(B) Copper

Ores—Copper is found free around Lake Superior in large quantities, and in small amounts in Cornwall and Siberia. One of the chief ores is cuprite, Cu_2O (cuprous oxide), in Cornwall, South America, and Australia. Other ores are copper glance, Cu_2S (cuprous sulphide); malachite, $CuCO_3Cu(OH)_2$; azurite, $2CuCO_3Cu(OH)_2$. It is also found in conjunction with iron in the beautiful pentagonal pyrites ($Cu_2SFe_2S_3$), sometimes mistaken for gold.

Copper compounds occur in minute quantities in the red colouring matter of certain feathers.

Production of Copper—The production of pure copper is much more difficult than that of iron, and this is the reason why the ancients knew brass and bronze but not copper.

The difficulty is due to the fact that copper is more fond of sulphur and less fond of oxygen than the other metals in its ores.

1. The ore is first slightly heated in the presence of coal. This causes part of the sulphur and the arsenic to pass off as oxides. Sufficient sulphur is retained to form cuprous sulphide, Cu_2S.

The temperature is then increased to melting-point, when any iron present enters into combination with the sand and is drawn off as slag.

The copper then consists of Cu_2O and Cu_2S.

2. The temperature is now raised, and these two compounds react.

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2.$$

3. The crude copper is drawn off and calcined as it contains both iron and sulphur.

The purest copper is obtained by the electrolytic process, carried out on a large scale. It simply consists of using impure ingots as anodes, and thin sheets of pure copper as kathodes, in a solution of $CuSO_4$ (copper

sulphate) slightly acid. The impurities drop to the bottom, and pure copper is deposited on the kathode.

(C) Lead

Ores—The chief ore of lead is galena, PbS, which is worked in Flintshire, the Lowther Hills in Scotland, the Hartz Mountains, Spain, Belgium, America, Australia, and Africa.

Other ores are anglesite, $PbSO_4$; cerussite, $PbCO_3$; and pyromorphite, $3Pb_3(PO_3)_2PbCl_2$.

Working—The extraction of lead from galena will be described.

1. First, the ore is heated to a moderate temperature in a reverberatory furnace. The sulphide is oxidized.
   (1) $2PbS+3O_2 \longrightarrow 2PbO+2SO_2$.
   (2) $PbS+2O_2 \longrightarrow PbSO_4$.
2. The temperature is raised, and some of the remaining sulphide reacts.
   (3) $PbS+PbSO_4 \longrightarrow 2Pb+2SO_2$.
   (4) $PbS+2PbO \longrightarrow 3Pb+SO_2$.
3. The molten lead is then run off.

Lead is one of the most useful metals in the service of man, its only drawback being its highly poisonous character. Water, for instance, which has stood in lead pipes should never be drunk, as it has the property of dissolving lead in minute quantities. The antidote for lead poisoning is dilute sulphuric acid, which is also injurious to the system.

Lead compounds form the basis of most paints and are nearly all poisonous.

5. Summary

1. *History*—Oldest in the service of man. Silver mines of Nubia under Rameses II. Idea of ancients: formed by

penetration of air into earth. Bible metals. Search for philosopher's stone. Tin and iron of this country.

2. *Properties*—Show several, including mercury. Refer to chief physical properties. Rarely found native—ores—why? Mostly fond of oxygen or other substances.

1. Burn several in oxygen. Rusting of iron, etc. Idea of calx or oxide.
2. Burn some in chlorine. Idea of a chloride.

3. *Action of Acids*—

1. Act with HCl and H_2SO_4 on metals and produce salts—soluble and insoluble.
2. Salts as a source of metals.

4. *Common Ores and Metals*—

1. Iron ore. Blast furnace.
2. Copper ore. Melaconite (CuO). Reduce by hydrogen.
3. Galena, PbS. Description of reduction. Red lead, Pb_3O_4, and its reduction by blow-pipe. Paint—white lead.

6. Results

(A) *Ideas*—

1. Metal and non-metal.
2. Chemical and physical properties.
3. Action of metals on acids.
4. Salts.
5. Alkalies.
6. Reduction of ores.

(B) *Substances*—

1. Various metals and their ores.

CHAPTER VII

SUGAR—STARCH

1. Sugar: Occurrence

Sugar is an essential food of animals. Without it we could not long survive. The elements of which it is composed are abundant—carbon, hydrogen, and oxygen; moreover, the hydrogen and oxygen are in the same proportions as they occur in water. Yet we cannot build up this substance, neither by our animal system nor by artificial means. Plants alone are able to do this for us. Thus sugar and starch occur only in the plant kingdom.

There are three chief sources of sugar:

(*a*) The sugar-cane industry is carried on in tropical and subtropical countries. The canes are cut and pressed between rollers. The juice is then refined by boiling, and the colouring matter removed by animal charcoal. In the refining process multiple evaporators, as shown in Chapter V., are used. The residue is called molasses, and sold as food, and for use in making cakes and toffee. Another by-product is syrup, used as a confection. Some forms of sugar, such as Demerara, contain a certain quantity of this syrup.

(*b*) Difficulties arose in the production of sugar during the American Civil War, and in consequence the sugar beet industry was enormously

increased. This is a white beet, grown largely in France, Belgium, and Germany. In all these countries the Governments granted bounties for the growing of the beet.

(*c*) A certain amount of sugar is also produced from the maple-tree in Canada in the early part of winter. The tree is tapped near the base, and the sugar-juice collected and sugar extracted.

The difficulties experienced during the war were largely due to the stoppage of the beet industry, as well as the shipping difficulty. No substitute ever produced can take the place of actual sugar, which not only has sweetening properties but many others which are essential to cooking. The minds of research chemists were largely directed to the spheres of explosives and gas, or some method of building up sugar might have been discovered. Economically, such a discovery may be of little value, as it does not seem that the natural means of production could fail; but in time of war it would be very useful to such a country as our own.

2. Experiments

1. Heat some cane sugar in a test-tube. It melts at 160° C., and at 215° C. decomposes. Note the change of colour. The substance remaining is caramel or burnt sugar, and is used for colouring soups and gravies and in the manufacture of sweets and toffee.

2. Heat some cane sugar, and note that water comes off, and finally the sugar chars.

3. Add some strong sulphuric acid to sugar on a tray. Note that a black substance remains. Wash this, and show that it is charcoal. Sugar may be written as $C_{12}H_{22}O_{11}$, and contains 11 molecules of water. The strong sulphuric acid takes up this water, leaving the carbon.

4. Heat some cane sugar with Fehling's solution. Fehling's solution is a mixture of copper sulphate and Rochelle salt, which is sodium and potassium tartrate. Note that there is no change in the blue colour.

5. Take some glucose, and heat with Fehling's solution. Note the formation of a red precipitate (Cu_2O) (cuprous oxide).

6. Heat some sweets with Fehling's solution, and see that Cu_2O is formed again.

7. Heat some sugar with dilute hydrochloric acid, and then test with Fehling's solution, and see that glucose is present.

Sugar, when heated with dilute acids, turns into "invert sugar." This consists of two other sugars, glucose and fructose:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}.$$

In formulæ these appear to be alike, but they vary in some of their properties, and the real difference is in their constitution. This action of inverting sugar, or hydrolysis, is the basis of most cooking operations and of fermentation.

Fructose occurs naturally in most fruits, and especially in the grape; also in honey, and gives the reaction with Fehling's solution.

8. *To make Sugar-Candy*—Make a concentrated hot solution of sugar and suspend a string in it while cooling. The result is sugar-candy.

9. *To make Sweets*—Take $\frac{1}{4}$ lb. of butter, and melt by means of a uniform heat, such as a gas-stove. Add any flavouring required. Now add 1 lb. of crystalline sugar, and stir for ten minutes until the sugar has absorbed the butter and is molten. Pour out on to a sugared board, and roll in strips, or pull; then cut into convenient sizes.

3. Milk Sugar

1. Introduce some rennet to some cow's milk. Note the formation of curds and whey. From the curds make cheese by pressing out the whey.

2. Evaporate the whey with a gentle heat and obtain a white powder. This is sweet to taste, though not so sweet as cane sugar. It is *milk sugar*. It is made up of carbon, hydrogen, and oxygen in exactly the same proportion as cane sugar, but it differs from cane sugar in several respects:

(*a*) It is not so sweet.

(*b*) It is more easily digested.

(*c*) On hydrolysis it gives glucose but not fructose, but a substance called galactose.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(galactose)}}{C_6H_{12}O_6}.$$

(*d*) It gives the reaction with Fehling's solution.

(*e*) When acted on by bacilli taken from cheese it produces lactic acid.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 4C_3H_6O_3 \text{ (lactic acid)}.$$

This explains why milk goes sour.

The difference between lactose (milk sugar) and cane sugar must be one of arrangement inside the molecule.

4. Grape Sugar (Glucose)

This sugar occurs in honey and fruits, and is the chief constituent of corn syrup. It is used largely for brewing and for the manufacture of sweets. It is usually brown in colour, though it should be white if pure. It is very sweet to taste, but is unsuitable for many cooking purposes for which cane sugar is used—*e.g.*, it is impossible to make jam with glucose alone. It was, however, largely used for domestic purposes during the war.

1. Test some glucose with Fehling's solution, and note the red precipitate.

2. Heat a solution of cane sugar with dilute hydrochloric acid, and note the formation of glucose.

3. Heat some milk sugar with dilute hydrochloric acid, and note the formation of glucose.

4. It is also obtained by heating starch with dilute hydrochloric acid.

$$C_6H_{10}O_5 + H_2O \longrightarrow C_6H_{12}O_6.$$

The action of dilute acids is to hydrolyze—*i.e.*, to put in water.

5. Starch

1. Starch occurs in all seeds and tubers. It is present in most plant life, and is probably one of the stages through which the plant builds up sugar for its food. Whatever the process is by which the plant builds up ordinary sugar from starch, we have not yet discovered it, and it is still impossible to produce cane sugar starting with starch, though glucose can be made by heating starch with dilute acids.

2. Cut a potato in two and dip into a basin of water. Rub the two halves together over the water and continue the process. The water becomes cloudy. Filter and dry the filtrate in a steam oven. Starch is produced. Starch can also be produced by a muslin bag containing flour being dipped in water and squeezed. The substance remaining in the bag is gluten (about 12 per cent.).

3. In manufacturing starch corn is soaked in water and then coarsely ground, the germ escaping the crushing. The mass is now mixed with water and the germ floats, and is skimmed off. The remainder is then finely ground. It contains three things—

(1) Bran.
(2) Gluten.
(3) Starch.

The fine powder is mixed with water and passed through a cloth sieve. The bran is thus separated. The water, containing gluten and starch, is then allowed to run down a slope, and the flow regulated by the slope. The starch, being heavier, sinks to the bottom, and is afterwards dried.

4. Examine starch under a microscope, and note its granular structure. Heat with water, and then examine. The granules disappear, and the starch is partly soluble. Hence the necessity for cooking starchy foods.

5. Place some starch (covered with saliva) in a warm place for half an hour. Test with Fehling's solution. It will be found that glucose is present. Saliva changes starch to glucose; starch as such cannot be digested, but glucose can. Thus starch left on the tongue turns sweet.

6. Take a solution of iodine in a test-tube and add starch solution. Heat, and the iodine is turned blue. This is the characteristic test for starch.

7. Add very dilute nitric acid to some starch in a porcelain dish, and heat in an air oven, keeping the temperature at 150° C. The starch changes into a glassy substance, yellow in colour. This substance is soluble in water, and is called dextrin, or gum. It does not react with Fehling's solution or iodine.

8. If the temperature be increased above 150° C. glucose will be formed.

$$\underset{\text{(starch)}}{C_6H_{10}O_5} + H_2O \longrightarrow C_6H_{12}O_6.$$

6. Summary

1. *Sugar*: *Occurrence*—Plants, cane, beet, maple, manufacture.

   Experiments—

   1. Heat—melts 160° C.; 215° C. decomposition forms *caramel* (burnt sugar for colouring). Sweets and toffee.

2. Heat—show water coming off. Char.
3. Strong H_2SO_4. Wash—charcoal left.

Test—

1. Fehling's solution—cuprous oxide on heating with *glucose.*
2. Test sweets, candy, etc.
3. Cane sugar; no action.

2. *Milk Sugar—*

1. Introduce rennin, and make *whey*—cheese. Evaporate whey and get milk sugar. Why does milk go sour? Sugar becomes acid. $C_{12}H_{22}O_{11} + H_2O \rightarrow 4C_3H_6O_3$ (lactic acid).

3. *Grape Sugar* (glucose). In honey, fruits, corn syrup.

1. Heat solution of sugar + HCl. Get dextrose or glucose. Test by Fehling's solution.
2. Heat starch with HCl and water—get dextrin and then glucose. $C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6$ (glucose).

Test by Fehling's solution.

Use of glucose in jam, jellies, beer. (White when pure).

4. *Starch*—In seeds and tubers.

1. Make starch from potato and flour. Refer to commercial process from corn.
2. Granules. Heat with water and show partial solubility, hence necessity of cooking starchy foods.
3. Test by iodine.
4. Heat starch and form dextrin—sweet.

7. Results

(A) *Ideas*—

1. Construction of molecules.
2. Hydrolysis.
3. Wonders of natural processes.

(B) *Substances*—

1. Cane sugar.
2. Glucose.
3. Milk sugar.
4. Fehling's solution and its reactions.
5. Starch and its reactions with iodine.

CHAPTER VIII

WOOD, PAPER, COTTON, ETC., CARBON

1. Introduction

Since the days of the Roman occupation of this country an industry has steadily proceeded without break in certain districts, such as the Lake District. This industry consists in cutting down young trees in autumn, stacking them in cones, covering these with turf, and burning the wood during the winter. The combustion is very slow, and little air is admitted. The result is charcoal, which was used by the Romans for fires and for smelting iron. Before the days of the Romans this fuel was known, and was probably prepared by the Egyptians. Now it is largely used in the manufacture of gunpowder and for domestic purposes.

In appearance charcoal corresponds to soot, which is obtained by burning coal, and is in effect mostly pure carbon.

Now examine several substances produced from plants or animals, such as various kinds of wood, cotton, silk, wool, feathers, paper, bones.

Heat each substance in turn in a test-tube, and note in each case that water comes off, also that a charred mass remains corresponding to carbon. It will also be noted that each has a special odour.

All these substances, taken from living matter contain carbon. Carbon is one of the chief constituents of all living things, and is essential to life. In most plant struc-

ture it is present in the form of cellulose, a fibrous substance of the same composition as starch, but with a larger molecule, so that it may be written $n(C_6H_{10}O_5)$ where n is undetermined.

2. Wood

Wood may be investigated (1) *botanically* by the use of microscope; (2) *chemically*, by analysis.

1. The microscope shows wood to possess the porous or cellular structure common to all living plant matter, enabling sap to reach the vital parts, and corresponding to the arteries and blood in man.

2. Analysis shows wood to contain about 50 per cent. carbon. By heating wood it is possible to convert it into charcoal, which is an impure form of carbon.

The carbon in wood is got from carbon dioxide in the atmosphere by a process of breathing through the leaves of a tree comparable to the lungs in animals. This gas is breathed into the atmosphere by animals, and is also formed whenever plant or animal matter is burnt. Carbon is an essential constituent of all living matter, and thus determines the interdependence of the plant and animal worlds.

Experimental—(1) Show that carbon dioxide is present in small quantities in the atmosphere, and in larger quantities in the exhaled breath, by means of lime-water.

(2) Show that carbon dioxide is formed when charcoal burns. The woody cell matter of trees and plants is composed of cellulose, a substance of great industrial importance. Its value depends on the fact that (*a*) it has a fibrous natural structure, enabling it to be made into sheets of paper; (*b*) it is chemically inactive—*i.e.*, durability; and (*c*) it is soluble in certain liquids. The finest form of natural cellulose is cotton (90 per cent. cellulose). Cotton fibres are longer than woody fibres (varying from

2 to 3 mm. in length), and hence make paper more readily; but the supply of cotton waste is unequal to the modern demand for paper.

3. Paper

The art of making paper consists in isolating cellulose fibres from vegetable matter, separating them from each other, and then uniting them to form a sheet. This may be done by steaming wood-pulp in the presence of alkali, collecting the fibres in a thin layer on an endless moving piece of gauze, and rolling the resultant sheet to the required thickness. The paper thus obtained is porous like blotting-paper. It is strengthened and made impermeable to ink by filling up the pores with some finely divided powder, such as china-clay, and with other sticky materials—operations known as loading and sizing.

Parchment Paper is non-porous. A piece of ordinary blotting-paper can be converted into parchment by dipping it into concentrated sulphuric acid, an operation which causes the cellulose fibres to swell and fill up the pores.

Other Products of Cellulose—

1. Gun-cotton, or smokeless powder.

By the action of concentrated nitric and sulphuric acids on cellulose, nitro-cellulose, or gun-cotton, is obtained. The H_2SO_4 (sulphuric acid) is only necessary to take up the water formed.

$$C_6H_{10}O_5 + 2HNO_3 \longrightarrow 2H_2O + C_6H_8O_3(NO_3)_2.$$

This substance is stable to heat, but explodes when in the presence of and by the detonation of a more sensitive explosive, such as fulminate of mercury. In modified form it is used in modern warfare as a propellant—*i.e.*, the substance placed in the breech of the gun which propels the missile. The fact that the products of such explosives are all colourless gases has revolutionized war.

Experimental—Soak some cotton-wool in a mixture of concentrated sulphuric and nitric acids for twenty-four hours and show that gun-cotton is formed.

2. *Artificial Silk*—By dissolving nitrocellulose in certain solvents and squirting the solution through fine openings, threads or filaments are obtained which, by suitable chemicals, may be reconverted into cellulose. The product has a beautiful lustre, is nearly as strong as silk, and is now manufactured in large quantities as artificial silk. Solutions of cellulose are also used for making photographic films.

3. *Artificial Leather* is obtained by mixing nitrocellulose with linseed oil and spreading the result on a fabric.

4. *Celluloid* is a mixture of nitrocellulose and camphor. It makes imitation bone, ivory, tortoiseshell, agate, etc. Its ready inflammability has now been overcome by the use of cellulose acetate.

5. By treatment of cellulose with dilute acids glucose is obtained, a substitute for sugar, and this can be fermented like sugars to alcohol. The industrial possibilities of a cheap supply of alcohol from vegetable refuse are enormous.

4. Bones

Bones are a mixture of earthy matter (calcium phosphate) and gelatinous animal matter. By heating bones the latter is carbonized in a finely divided state to animal charcoal. This is used extensively on account of its power of absorbing obnoxious gases and impurities in solution, such as in purifying sugar, in sewers, etc. An unexpected use was its employment in the box respirator, where it was the active agent in rendering this a protection against all the poisonous gases invented by German ingenuity.

Experimental—Show the absorption of ammonia or H_2S by charcoal over mercury or of colour by boiling the powder with indigo solution.

5. Carbon

Carbon is one of the commonest substances occurring in Nature. Not only is it present in all living matter, and appears in the form of charcoal when this matter partially burns, but it is contained in large quantities in mineral oils, and is deposited when they burn with an insufficient supply of air. Besides this it appears in two other forms as a mineral.

1. Graphite, which is found largely in Ceylon, Cumberland, and Austria.

2. Diamond, which occurs in most meteorites, and is found in conjunction with iron deposits in Africa, India, and America.

Of all the three forms the diamond is the purest. The diamond and graphite are both crystalline in character but of different structure.

Graphite is a black shiny substance and fairly soft. It is used largely in the manufacture of pencils and for the preparation of certain black-leads. It is now also used in the preparation of certain gunpowders.

For the manufacture of pencils it is first crushed and then mixed with water to form a paste. This paste is passed through machines, which finally turn it out in circular strips. These strips dry naturally in a well-heated room, and are then placed in the wood casing of the pencil. There are excellent works at Keswick, where the plumbago or graphite is brought from Borrowdale.

Diamond—Lavoisier proved that the diamond was carbon by burning one, and showing that there was no residue and carbon dioxide was formed.

Many attempts have been made to produce diamonds

from ordinary carbon, and have met with some success, though the diamonds produced are useless as gems because they are never obtained free from black spots.

Moisson, a French chemist, in 1887, was the first to perform this. He knew that diamonds were always associated with iron, so heated iron and charcoal together in an electric furnace. The charcoal dissolved in the molten iron as sugar dissolves in water. He then cooled the iron by dropping into water, but could not get sufficient cooling because a steam jacket was formed by the molten iron

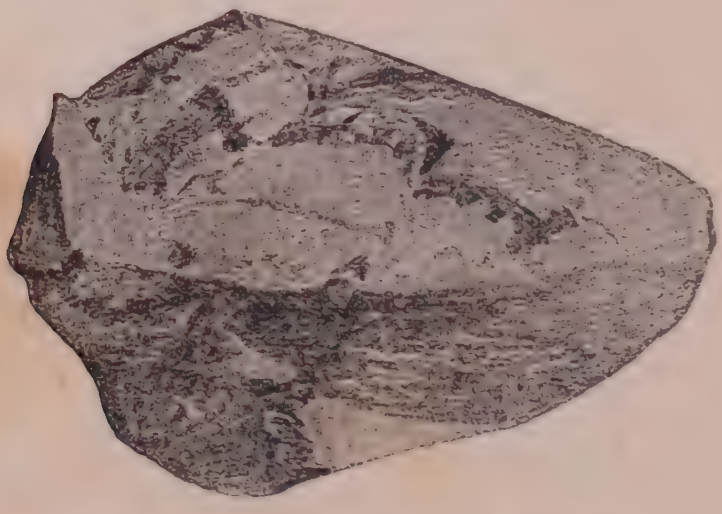


Fig. 16—The Cullinan Diamond

and slowed down the cooling. He then first dropped the molten iron into molten lead, and then into water. In this way, the iron cooling first on the outside, contracted, and thus exerted enormous pressure on the dissolved carbon. On cooling this solidified out under the enormous pressure, the result being small diamonds containing black spots of non-crystalline carbon. If the temperature could be raised and the pressure on cooling increased, we should then get clear diamonds. This method of Moisson's probably approximates to that of Nature in forming diamonds.

The small diamonds are used for glass-cutting, as the diamond is one of the hardest substances known.

The diamond as found naturally is not usually brilliant. It requires polishing and cutting. This industry is almost confined to Amsterdam, and a few Dutch and Belgian towns. The largest natural diamond is the Cullinan, found in the Transvaal, and presented to King Edward VII. Another famous diamond is the Koh-i-noor, which came from India.

Amorphous Carbon—*i.e.*, shapeless carbon. This occurs in many forms, mostly impure, such as:

Coal.	Lampblack.
Lignite.	Bone carbon.
Peat.	Wood charcoal.
Soot.	Coke.

Lampblack is the purest form of amorphous carbon. Another pure form is obtained by the action of strong sulphuric acid on sugar. The water is taken out and carbon left.

Carbon has many uses, the chief of which are:

1. Manufacture of gunpowder (used in the form of wood charcoal).
2. Domestic purposes, such as irons for clothes, stoves, braziers.
3. Uses depending on its absorption properties:
   - (*a*) Disinfectant for drains.
   - (*b*) In box respirators.
   - (*c*) In refining sugar, etc.
   - (*d*) In household filters.
4. For reducing metals.

Place some red lead on a charcoal block and heat in a blowpipe flame. Lead is produced.

Carbon is one of the substances which can exist in more than one state or form. This property, which is possessed by other substances, such as sulphur and tin, is called allotropy. The whole process of allotropy is but little understood, but it is almost certain that the difference is due to physical conditions of temperature and pressure, and is largely the result of the slowing down of the rate of change. One form of carbon must be the normal form at ordinary temperature and pressure. The others must be artificial for the same conditions, but the rate at which they change to the normal form must have been enormously slowed down, perhaps by sudden cooling under enormous pressures.

When we are able to produce greater temperatures than we are at present, and to imitate some of the enormous natural pressures, it may be possible to produce diamonds from soot quite readily, for the conditions necessary are known to the physical chemist.

6. Summary

1. *Introduction*—Refer to charcoal burners. Introduce several substances all derived from living organisms, plant or animal. Heat each substance in turn, and note (1) water; (2) carbon left; (3) peculiar odours. Each contains water and carbon.

Substances taken: Wood (various kinds), cotton, silk wool, feathers, paper, bone.

2. *Wood*—Botanical structure—chemical analysis.

3. *Paper*—Manufacture from wood and cloth. Basis is *cellulose*. Describe manufacture.

Cellulose—

1. Show will not dissolve in water. Alcohol and dilute acids.

2. Action of strong H_2SO_4—

$$C_6H_{10}O_5 + H_2O \longrightarrow C_6H_{12}O_6 \text{ (dextrose)}.$$

3. Action of strong HNO_3 gives gun-cotton.
4. Nitro-cellulose + camphor—→ celluloid.

4. *Bones*—Production of animal charcoal.

5. *Carbon*—Show three forms. Refer to coal, lignite, anthracite.

1. Make charcoal from wood and sugar.
2. Absorbing gas and colouring matter (several experiments). Thus: respirators, filters, drain-traps.
3. Reducing action—blow-pipe.
4. Burning forming CO_2.

7. Results

(A) *Ideas*—

1. Allotropy.
2. Carbon essential to life, and the interdependence of plant and animal life.
3. The necessity of fibrous matter and its effect on varying structure.
4. Reduction.

(B) *Substances*—

1. Cellulose and its modifications.
2. Gun-cotton—celluloid—paper.
3. Graphite.
4. Diamond.

CHAPTER IX

COAL

1. History

Coal seems to have been known from very early times, though little used. Probably the first coal discovered may have been sea-coal—that is, coal found on the sea-shore owing to the outcrop of the seam.

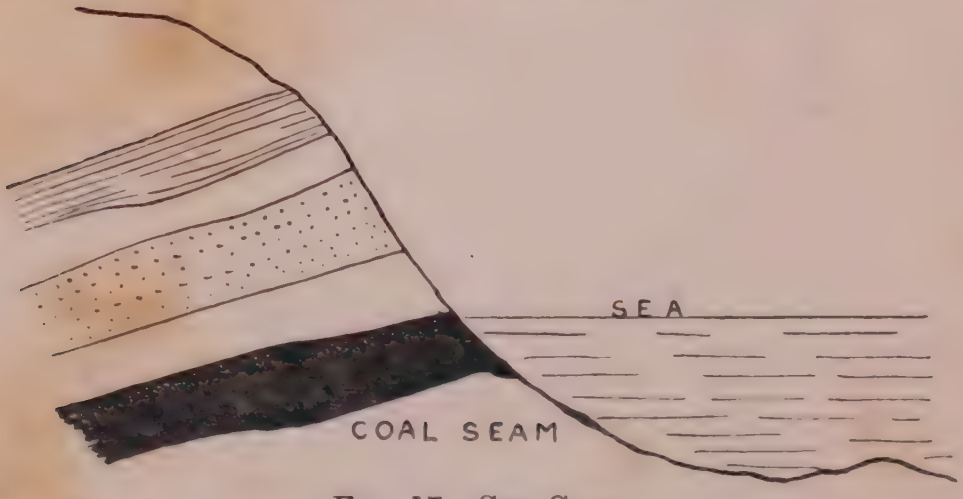


Fig. 17—Sea-Coal

But such outcrops occur inland also, especially in such localities as Wigan, where they are the result of a fold in the earth's surface called an anti-cline.

It must have been from these outcrops that men first obtained coal, and its inflammable character may have been discovered by the accident of using it as other stones were used for building fireplaces.

It is generally agreed that the "Lapis Ampelites" of the Romans was our cannel coal; but they used it for

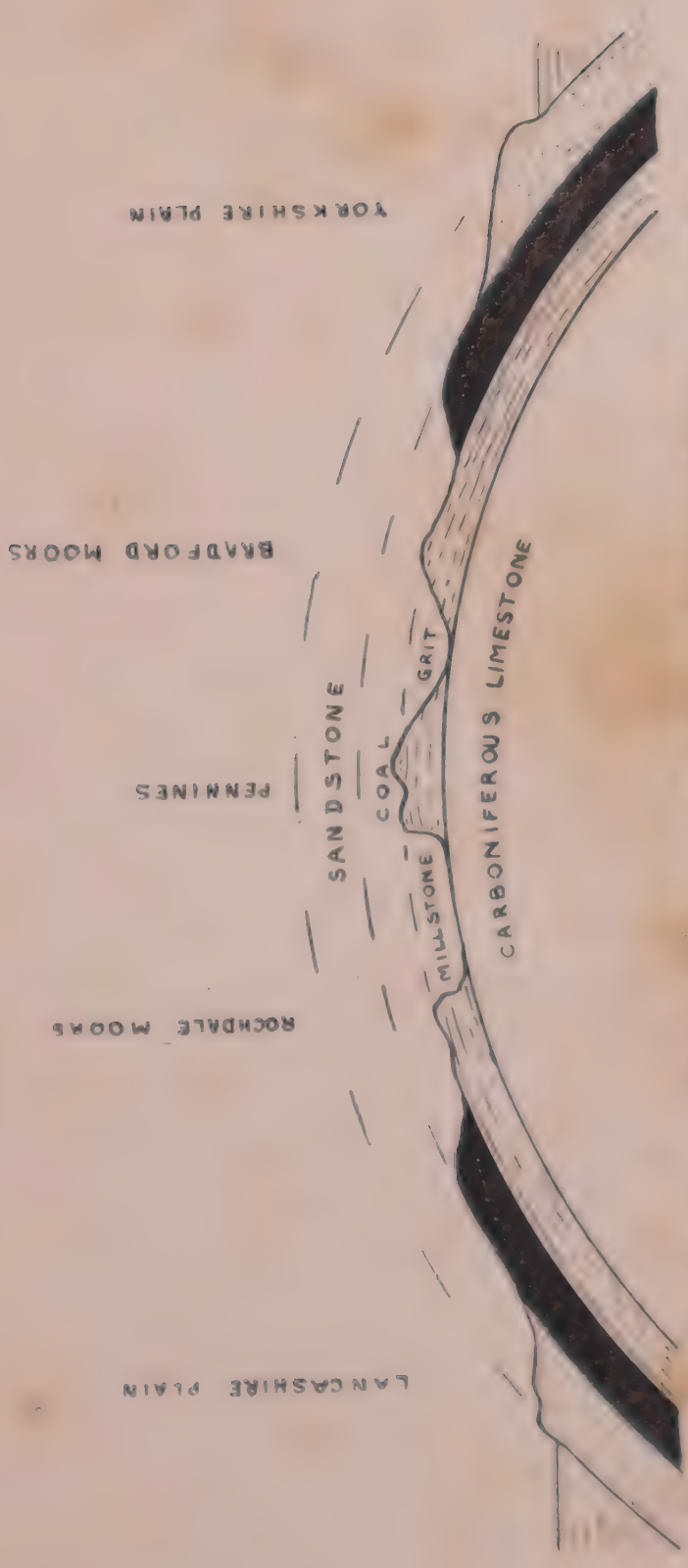


FIG. 19.—SECTION ACROSS LANCASHIRE AND YORKSHIRE SHOWING OUTCROP OF ROCKS

making beads and toys. The Ancient Britons used coal in the districts where it was brought down from the moors in the fast-flowing streams. Some years ago several pieces were discovered in the sand under the Roman Way at Ribchester, and there are many evidences of its use in the buried towns which line Hadrian's Wall on the Newcastle side. The very name itself is British and not Saxon. The Irish still use "O'guul" and the Cornish "Kolar."

Still wood continued to be used as the staple fuel. In 852 we find a grant of lands being made by the Abbey of Peterborough, and amongst the payments are 60 carts of wood and 12 carts of coal, proving that wood was still more used than coal, but that coal was mined by the Saxons.

In 1272 Henry III. granted a charter to the town of Newcastle to dig coal, and later this coal was brought by ships to London; but even in great halls wood still remained the chief fuel, as can be seen by an examination of Oxford Halls. New College Hall, built in the fourteenth century, is without a fireplace, and still has the "lantern" in the roof for the escape of smoke from the central wood-fire; so has Wadham; but halls built in the next century, such as Magdalen, have their fireplaces for burning coal.

Coals were not, however, brought into general use until the reign of Charles I. The reason for the formation of coal in the crust of the earth was long a matter of doubt, but geologists have come to the aid of chemists, and it is now proved that coal is merely the fossil remains of the luxuriant vegetation of great primeval forests. By process of pressure, extending through ages, a process of carbonization has been going on, and the cellulose has been reduced, the oxygen and hydrogen going to form gases such as methane and carbon dioxide, both of which are prevalent in mines as "fire-damp" and "choke

damp." If this is so we ought to find coal at varying stages of formation, and this we do, ranging from peat, through lignite and coal, to anthracite.

The following table will show how the process of carbonization has proceeded :

	Carbon per Cent.	*Hydrogen per Cent.*	*Oxygen per Cent.*	*Calorific Value B. Th. Units per Lb.*
Cellulose ..	44·5	6·2	49·3	7,500
Wood ..	50	6·5	43·5	7,450
Peat	57	6	37	9,850
Lignite ..	67	5·2	27·8	11,700
Coal	92·5	4·7	2·7	15,720
Anthracite ..	95	3	2	16,000

Another clear proof that coal was once vegetable matter is given in the existence of fossil remains in coal. Some years ago at Wigan a whole tree-trunk, perfect in shape, was dug up, and the fronds of ferns are very common.

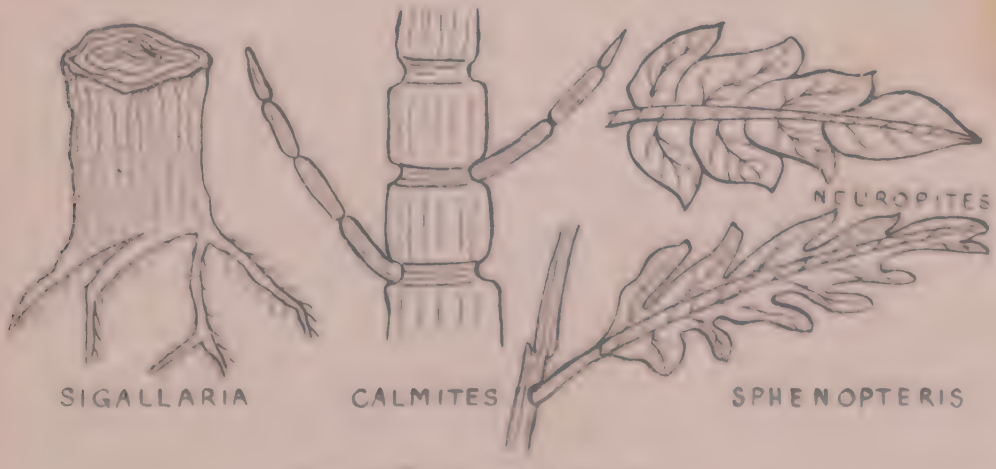


FIG. 19—FOSSILS IN COAL

It must not be thought that coal is a definite chemical compound. Different coals vary in their composition enormously, and it must rather be regarded as a complex mixture of chemical compounds.

2. Occurrence

Coal occurs almost universally, but there are some countries richer than others. Our own country, for instance, is one of the richest coalfields, and has been taxed to its utmost during the Great War, as the coalfields of Belgium and those of Northern France were in German occupation.

During the last century there has been an enormous demand on coal, owing to the industrial changes, and at present we alone produce 290 million tons annually. Authorities are divided as to the time that the coal will last, but 350 years is the maximum. At the end of that time some new source of energy will be required, and it remains for the ingenuity of scientists to develop this for the generations to come. The importance of scientific research is not always realized, especially by literary people, and never until recently by the Governments of our own country.

How can we diminish the consumption of coal without loss of energy? There are many ways, but sentiment is strongly entrenched against the adoption of them. Domestic heating in Great Britain takes 40 million tons annually. The open fire is the most wasteful form of consumption, for one-third of the heat is taken in distillation of the gases contained in the coal. It has, however, its advantages, such as its provision of ventilation and its cheerfulness. Distilled coal would, therefore, be best for burning in the open fire, but unfortunately this material (coke) will not readily burn except in a stove. Coal, however, distilled at a lower temperature is smokeless, and will burn in an open grate. This material known as "coalite" has been produced, and should prove very valuable in the future in reducing the waste of coal energy in the open grate.

"Central heating" would be the best solution of the difficulty, and it has been adopted in some flats in larger towns.

The use of gas for cooking and heating is a great saving in fuel energy, and should be encouraged by the reduction of illuminating power (now rendered unnecessary by the use of mantles) and the consequent increase in heating power of our town gas supplies. Gas companies and corporations should move in this matter.

The use of oil and peat as fuels will also help. The area of available peat in Europe has been estimated at 140 million acres, and Ireland has peat equivalent to 2,500 million tons of coal.

3. Action of Heat

1. Heat a piece of coal in a Bunsen flame and note:
   (*a*) The softening.
   (*b*) A gas given off.
   (*c*) The gas burns, as does the solid part.
   (*d*) Ash is finally left.

2. Burn some coal in a jar of oxygen and test for water and carbon dioxide.

Fig. 20.—Heating Coal in a Hard Glass Tube

3. Place some coal in a hard glass tube, slightly sloping, as shown, and distil by heating with Bunsen burners. Test the gas coming off:

(*a*) Smell. Note the smell of rotten eggs. This gas is sulphuretted hydrogen (H_2S), and has very bad effects when in coal gas, as it burns producing sulphur dioxide (SO_2), a gas which gives a choking sensation, and is poisonous.

(*b*) Note the gas burns with a blue flame if coming out of a fine hole, but is luminous otherwise.

(*c*) Test with red litmus paper, and it may turn blue owing to the presence of ammonia.

(*d*) Pass into lime-water, which is turned milky, showing the presence of carbon dioxide.

Note that at *A* a thick black semi-liquid forms. This is coal-tar.

Examine the residue in the tube and note its hardness and sponge-like appearance. This is coke.

4. Coal Gas

The first use of coal gas was by Lord Dundonald, in 1776; but it was not used for lighting purposes until 1792, when a man named Murdoch lighted his house with it and was accounted a fool. In 1810, however, London Bridge was lit by gas lamps. Until that time candles, pine-torches, rush-lights, and vegetable oils were the only sources of light.

Coal then was distilled in large quantities for the sake of producing this gas, but all the other substances that we have seen come off were allowed to escape in some cases and in others wasted. So great, however, has been the march of chemical progress that now the by-products are more valuable than the coal gas. These gases and liquids are abstracted from the coal gas before it is circulated.

In the manufacture of gas, coal is heated in huge retorts to a temperature of 1,800° F., and the gases led away by

a pipe which dips under the surface of water in a tank. Here part of the *water* coming off and the *tar*, condense. The gases then pass through cooling pipes. Most of the *ammonia* has dissolved in the water, and the rest is removed by "scrubbers." The gases are next passed through trays containing slaked lime. This removes the carbon dioxide and the lime is then known as "gas lime." Gas lime is used as a manure. The sulphuretted hydrogen is then removed by passing over iron oxide, which is turned into iron sulphide.

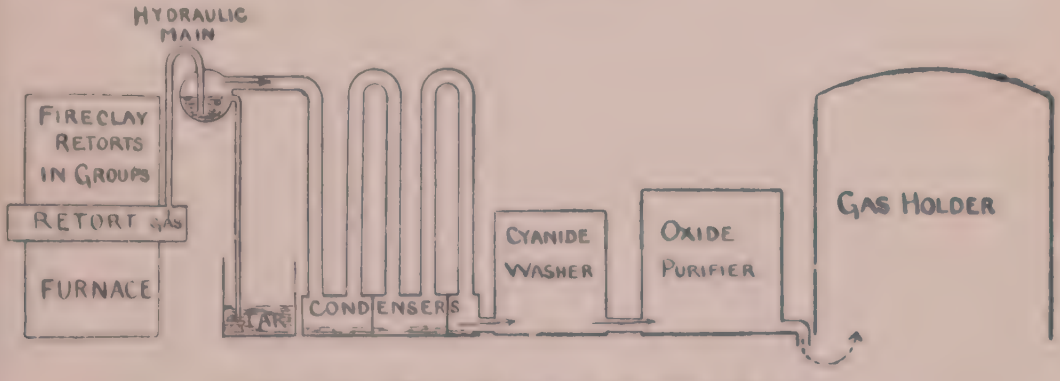


FIG. 21—GAS MANUFACTURING PLANT

In 1911 there were produced 1,111,800 tons of ammonium sulphate from the distillation of coal in this country. Coal-tar, which fifty years ago was a nuisance, is now one of the most valuable by-products, and is the source of benzene, phenol, naphthalene, cresol; and some of these, again, can be converted into explosives, dyes, flavours, perfumes, and drugs.

One ton of coal on an average will produce:

11,000 c. ft. of gas.
120 lb. coal-tar.
25 lb. $(NH_4)_2SO_4$ (ammonium sulphate).
1,500 lb. coke.

Coal-gas, as it is sent from the gasworks, varies in composition, but can roughly be divided into illuminants and non-illuminants, as follows:

Illuminants		*Non-illuminants*	
Unsaturated hydrocarbons, such as acetylene	4 per cent.	Hydrogen	49 per cent.
		Methane	35 ,,
		Nitrogen	6 ,,
		Oxygen	·5 ,,
		CO	5 ,,
		CO_2	·5 ,,

These unsaturated hydrocarbons provide the luminosity, and can be abstracted by passing coal gas through strong sulphuric acid. If this is done the gas will burn with a non-luminous flame. The presence of the hydrocarbons in the sulphuric acid can be detected by their peculiar odour.

5. Incandescence

1. There are two kinds of Bunsen flames, one light-giving and one not. Note that the light-giving flame deposits carbon on vessels put into it and the other does not. In the case of the real Bunsen flame the gas is mixed with air before burning. This suggests that the carbon is completely oxidized or burnt up because of the excess of air.

2. Note the structure of a candle flame. There is an outer portion of blue flame which gives little light. If a porcelain dish be introduced to this part of the flame no carbon is deposited. Here there is contact with the oxygen of the air, and complete combustion takes place.

There is next a large luminous cone, and if any white surface be introduced here carbon will be deposited, showing there is free carbon present. It must, however, be in a luminous or white-hot condition or it would appear black. If a piece of blotting-paper be brought down on the flame for a few seconds three definite rings will be obtained: first, an inner ring, perfectly white and unchanged; second, a black ring of carbon deposit; third, an outer charred ring. These correspond to the three parts of the flame.

The inner portion of the flame appears non-luminous,

and it can be shown to be merely a gaseous mass not brought up to the point of ignition. Place a match across the flame as shown, and no charring occurs where it passes through the inner portion. Insert a glass tube into this inner portion and apply a light to the other end. The gas being led away will burn.

Soak a piece of filter paper in mercuric iodide, a red substance, and allow it to dry. Bring this paper from above on to the flame, and two distinct rings will be formed. An outer ring of yellow and an inner one of red. Now, mercuric iodide is yellow at a temperature of 150° C., and we see this temperature is only reached in the two outer portions of the flame.

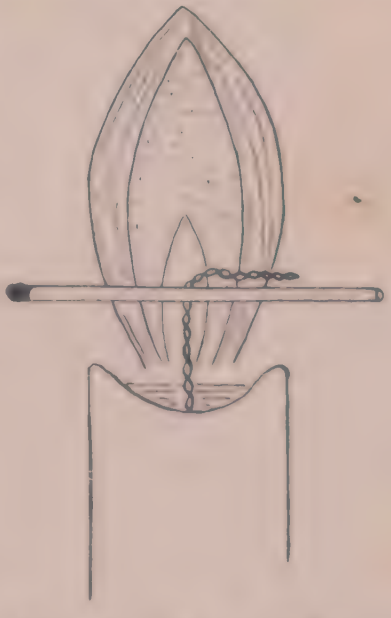


FIG. 22—FLAME STRUCTURE

It is evident, therefore, that what is burning is not the solid candle, nor the liquid fat, nor the wick, but gases made from the fat of the candle.

3. Why are some flames luminous and others not? This problem interested the minds of people over one hundred years ago, but little advance was made until the end of last century. In 1816 Sir Humphry Davy was the first to advance a theory, and he declared that the luminosity was due in all cases to the presence of solid particles in the flame, these particles being white-hot, or incandescent. But in 1845 Frankland showed that it was possible to have luminous flames where no solid particles existed—*e.g.*, hydrogen burning under pressure is luminous. This can easily be shown by drawing out a glass tube to a fine end and burning hydrogen at this fine end. Such luminosity is probably due to the presence

of dense unburnt gases or vapours in the burning part of the flame.

It is perfectly true, however, that the introduction of solid particles into a non-luminous flame—whether the solid is combustible or not—does cause luminosity. Everybody is familiar with limelight. It is also true that in hydrocarbon flames luminosity is caused by solid particles of carbon. Where does this carbon come from? Lewes has suggested it is due to the breaking down of acetylene, which must always be present. Acetylene is formed of equal parts of carbon and hydrogen, and as hydrogen is more easily oxidized a certain amount of carbon is set free. Whenever free acetylene is burnt and not supplied with free oxygen this always takes place. The luminosity of the ordinary coal gas flame is probably due to the presence of this acetylene.

The efforts to increase the luminosity of coal gas have been continuous. In 1829 Berzelius noted that the presence of thoria (a rare earth) gave increased luminosity. Magnesium oxide does the same, and so would lime if the temperature were sufficiently high, but for lime the oxy-hydrogen flame is required, and this is used in lanterns.

No further work was done until 1885, when Welsbach studied the rare earths, and as a result, in 1893, patented his mantle.

These mantles are made of knitted cotton or artificial silk. They are then washed thoroughly in dilute acid and water, and dipped in a mixture of 99 per cent. thorium nitrate and 1 per cent. cerium nitrate. They are then rolled and dried on a shape, and burnt. This converts the nitrates into oxides, and the organic matter is burnt away. They are then varnished for transport purposes. Before the war 250 millions were being made annually, and 50 millions in this country. They are now used not only for coal gas flames but with oil lamps.

The rings for inverted mantles are made of china clay and silica.

6. Ignition Point

1. Try to light the gas by a hot wire. It is impossible to do this. Try with a fusee match. This also fails unless the match is struck over the escaping gas.

2. Turn on a Bunsen burner, and hold a piece of wire gauze about 2 inches above. Light the gas above the wire gauze. It does not burn below, the gauze conducting away the heat of the flame above.

Every gas has a definite ignition point, and until this is reached it does not burn. On this principle is fashioned the Davy lamp. It merely consists of a flame surrounded by wire gauze. If explosive gases are outside they will not burn, although there is a flame inside the gauze, because the gauze is continually conducting away the heat, so that the ignition point of the outside gases is not reached.

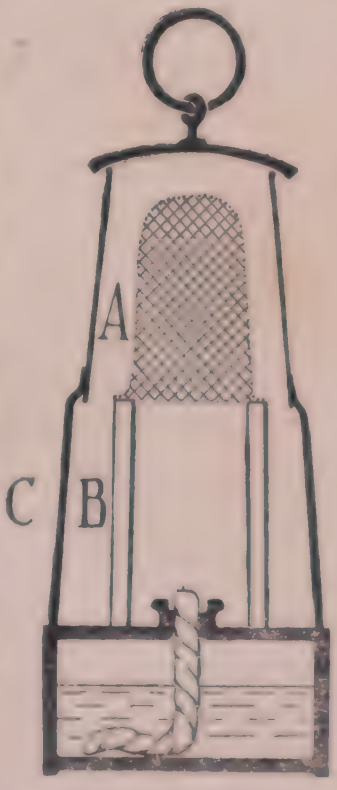


FIG. 23—THE DAVY LAMP

A = Fine wire gauze; B = glass; C = metal rods supporting the cap which protects the gauze.

7. Summary

1. *History*—Used by Britons—mined by Saxons.

2. *Occurrence*—Primeval forests: peat: lignite: coal: anthracite: mining fourteenth century.

3. *Action of Heat*—

1. Heat piece in flame—softening—gas—final burning—ash.

2. Burn in jar of O, and test for water and CO_2.
3. Distil from hard glass tube.

Note: (1) H_2S given off; (2) CO_2 given off; (3) coal gas; (4) ammonia; (5) coal tar; (6) coke.

4. *Coal Gas*—Describe manufacture. First used by Lord Dundonald, 1776. Murdoch, 1792, lighted his house.

1. Pass coal gas through strong H_2SO_4 and absorb. Ethylene and marsh gas. Burn at other end, and note difference.
2. Burn coke. Note blue flame of CO.

5. *Incandescence*—Note Bunsen burner—two kinds of flame.

1. Lead off gas from centre of flame and burn.
2. Repeat with candle.
3. Show black deposit of carbon in outer part by bringing paper down on flame.
4. Incandescent mantle.
5. Lime-light.

6. *Ignition Point*—

1. Try to light gas by hot wire.
2. Burn gas above wire gauze.

8. Results

(A) *Ideas*—

1. Flame structure.
2. Incandescence.
3. Ignition point.

(B) *Substances*—

1. Sulphuretted hydrogen.
2. Ammonia.
3. Coal tar.
4. Coal gas.

CHAPTER X

MINERAL OILS

1. Occurrence

These mineral oils, which are not oils in the strict chemical sense of the word, were unknown for all practical purposes until about 1840, when the shale industry of Scotland was developed.

It is true there were natural springs of this oil, sometimes continually burning; but these were merely the objects of fire-worshippers. Such were those near Baku, to which the Persian Guebers, or fire-worshippers, made pilgrimage. Marvin, in "The Region of Eternal Fire," 1884, describes the change brought about by the development of industry in this region:

"The worship of the Eternal Fire in the Surakhain temple is dead; the priest has left behind no followers; but the oil that dimly lit a shrine now illuminates an Empire, and bids ere long to give light and heat to an entire hemisphere."

Rider Haggard, in his "Ayesha," gives a very fine account of such a supposed shrine in Thibet.

This natural oil was probably used as a medicine at a very early date.

Now it is one of the most useful products of the mineral kingdom in the service of man.

The first industry to be developed was the shale of Scotland, started by James Young, in 1847. The sole object of the industry was to produce paraffin wax and

vaseline. The oils were practically discarded and sold to Germany for almost nothing. German ships waited at Scottish ports and took away the most valuable part of the shale. It was a German who first realized that this oil could be used in lamps, though a different lamp was required from that which burnt vegetable oils. This new lamp he invented.

Soon afterwards real oil springs were discovered in America, and the wells at Baku began to be opened. This meant serious competition for the Scottish industry, and it persisted only by dint of chemical ingenuity. In fact, its persistence is one of the greatest tributes to the advantage of chemical research in the furtherance of commercial enterprise.

Besides the industries in Scotland, America, and Southern Russia, we have large works in Galicia and Rumania. The German invasion of Rumania was largely for the purpose of exploiting the oil-fields. There are also fields in Mexico and Burmah.

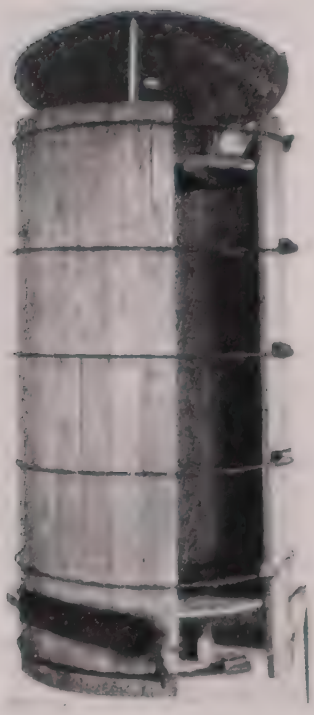
A great deal of discussion has taken place on the origin of mineral oils. An analysis shows that they are chiefly hydrocarbons—that is, mere compounds of hydrogen and carbon.

One theory is that they are the result of the action of compressed steam in the earth's crust on decayed marine matter of very early ages; but it is questionable whether such matter exists at such depths.

Another theory holds them to be the result of the action of water on various carbides in the earth's crust. Everybody knows that when water acts on calcium carbide the result is acetylene.

$$CaC_2 + H_2O \longrightarrow CaO + C_2H_2.$$

This acetylene is a hydrocarbon, and it is supposed that other carbides would form higher hydrocarbons.



A VINEGAR CASK

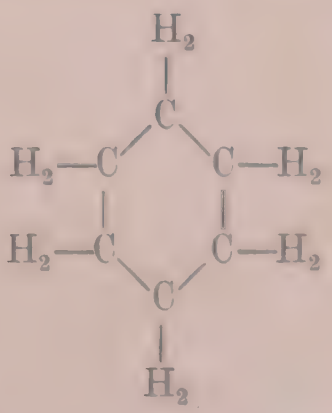
NEW OIL DERRICKS

2. The Industry

In Pennsylvania boring is carried out sometimes to a depth of 1,000 feet. At first the oil squirts up, but finally has to be pumped up. In Scotland the oil is found in shale, and the whole deposit of shale is taken up and distilled in air-tight retorts.

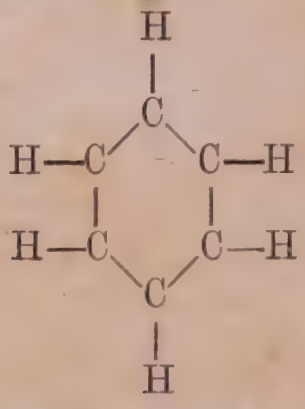
American petroleum is a thickish brown liquid, which consists of a number of hydrocarbons, ranging from those containing four carbon atoms to those containing twenty. Some natural oils contain hydrocarbons with thirty carbon atoms. All hydrocarbons with over sixteen carbon atoms are solid. The hydrocarbons divide themselves into four series:

1. Paraffin series, which can be generally written C_nH_{2n+2}, where n is any number from one to twenty. Methane, or marsh gas, is the lowest of these, and is written CH_4.
2. Olefine series, which can be written C_nH_{2n}.
3. Naphthalene series, which are also written C_nH_{2n}; but the molecule is constructed in the form of a ring.



C_6H_{12} Naphthalene is the lowest.

4. Benzene series, which can be written C_nH_{2n-6}.



Benzene is the lowest.

American petroleum has a preponderance of paraffins and Baku of naphthalenes. The lower the hydrocarbon is the more inflammable it is, and the lower its boiling-point. Thus it is possible to separate the crude oil into definite parts according to boiling-points by boiling at fixed temperatures. This method is called fractional distillation. The result of this is several commercial products, as follows:

(*a*) *Cymogene*—A gas which comes over at temperatures up to 8° C. It contains chiefly CH_4, C_2H_6, and C_3H_8.

(*b*) *Rhigolene*—Comes over at from 8° C. to 45° C. It is a liquid, and contains C_3H_8 and C_4H_{10}. It is most useful as a local anæsthetic, and is used by dentists.

(*c*) *Petroleum Ether*—Comes over at from 45° C. to 60° C., and contains C_5H_{12} and C_6H_{14}. It is also used as an anæsthetic.

(*d*) *Benzene*, or *Benzoline*—Comes over at from 60° C. to 120° C. It is known commercially as benzene, but ought to be called benzine to distinguish it from the real article, which is distilled from coal tar. This substance contains C_7H_{16}, C_8H_{18}, C_9H_{20}, and is used for dry cleaning.

(*e*) *Petrol*—Comes over from 90° C. to 120° C., and also

contains C_7H_{10} and C_8H_{18}. It is used as fuel for motors, and also for lighting country houses.

(*f*) *Kerosene* or *Paraffin Oil*—Comes over at 150° C. to 300° C., and is an almost clear liquid containing hydrocarbons up to C_{14}. It is used for lighting purposes.

(*g*) *Lubricating Oils*—Come over at a temperature of 300° C., and contain hydrocarbon of C_{15} and upwards.

(*h*) *Residue*—Is a thick substance, which will not distil without cracking, and when refined it forms vaseline and paraffin wax.

3. Analysis of Petroleum

1. Burn some petroleum in an open vessel and show the formation of carbon. Thus it is necessary to have a special lamp which supplies air to burn up the carbon. When the air is insufficient we get lampblack.

2. Burn a paraffin flame against a cold surface and collect the water formed.

3. Pass petroleum vapour over heated copper oxide in a hard glass tube. (In heating the petroleum care must be taken to exclude the air.) After passing over the CuO (cupric oxide), lead by a tube into a cooled flask, and show the formation of water. Then lead into some lime-water, and show by the milky appearance the formation of CO_2 (carbon dioxide). Thus petroleum consists of carbon and hydrogen.

Copper is left in the tube.

4. Mix petroleum vapour and air in a soda-water bottle and apply a light. They explode. When paraffin lamps were first introduced many explosions took place. This was due to the fact that the paraffin sold contained some low boiling hydrocarbons. These vaporized and mixed with air in the well. Now all paraffin sold must be above a certain flash-point—that is, it must not flash below the temperature given. The temperature is 73° F.

All oil lamps should have air excluded from the well and should have the well continually filled with oil. The presence of white fumes in the well is a sign of danger.

4. Marsh Gas

When explosions occur in mines they are caused by the presence of fire damp, or marsh gas. This gas, when mixed with air, is very explosive.

Marsh gas is usually found in stagnant pools—hence its name. At the beginning of the nineteenth century an old Quaker schoolmaster might have been seen in the

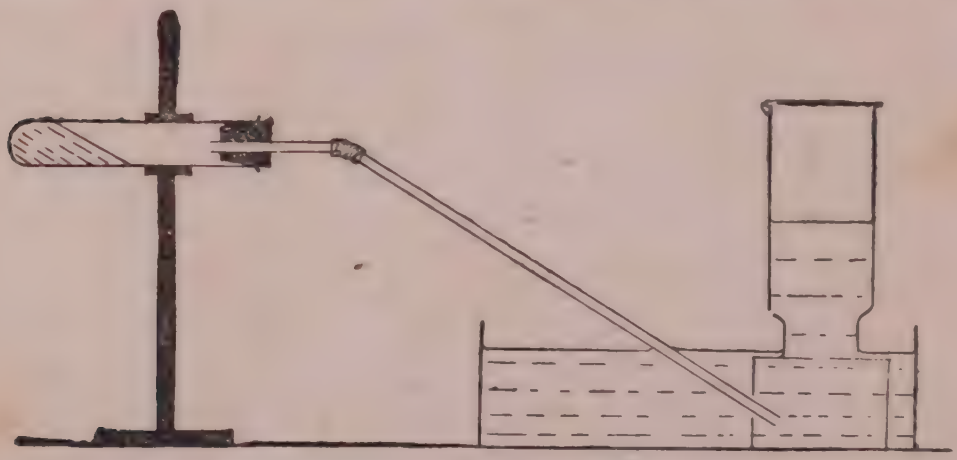


Fig. 24—Preparation of Marsh Gas

neighbourhood of Manchester poking pools with a stick and collecting gas from them in a jar. This man was John Dalton, a very eminent chemist.

1. Prepare marsh gas by heating a mixture of sodium acetate and sodium hydrate. The sodium hydrate must be anhydrous as well as the acetate.

$$CH_3COONa + NaOH \longrightarrow Na_2CO_3 + CH_4.$$

2. Burn marsh gas and show the production of carbon and water.

3. Explode a mixture of marsh gas and air in a soda-water bottle.

4. The nature of the safety-lamp has already been explained.

5. Acetylene

For many years acetylene has been used in bicycle and motor lamps, and is now used for house lighting purposes where gas is not available; but it is this substance present in coal gas which causes the luminosity of an ordinary gas flame. Both acetylene and marsh gas are present in small proportions in natural mineral oils, but must be got rid of in commercial paraffin.

1. Prepare acetylene by acting with water on calcium carbide. Calcium carbide is formed by heating coal and lime together.

$$4CaO+5C_2 \longrightarrow 4CaC_2+2CO_2.$$

This calcium carbide when acted on by water produces acetylene.

$$CaC_2+2H_2O \longrightarrow Ca(OH)_2+C_2H_2.$$

2. Burn acetylene, and show the luminous flame—the formation of carbon and water.

3. Now pass acetylene through a very finely drawn-out glass tube and burn. Note that the luminosity is increased and no carbon is deposited. It was the introduction of this very fine-holed burner which made lighting with acetylene possible.

4. Mix some acetylene with air and explode in a soda-water bottle. It is better to use pure oxygen, in the proportion of 1 part of acetylene to $2\frac{1}{2}$ parts of oxygen. Acetylene explodes more readily than marsh gas because it is unsaturated. Carbon really requires four atoms of hydrogen or their equivalent to satisfy itself, and if we write down acetylene as shown it will be seen that—

$$H—C \equiv C—H$$

four more atoms of hydrogen would be required to satisfy the two carbon atoms. Hence we conclude there is a weakness at the triple link.

5. Many explosions occurred in the early days of acetylene lighting, due to the use of brass or copper burners; for copper readily combines with acetylene to form cuprous acetylide, a substance which is so unstable that if scratched by a knife it will explode. Now special non-metallic burners are prepared.

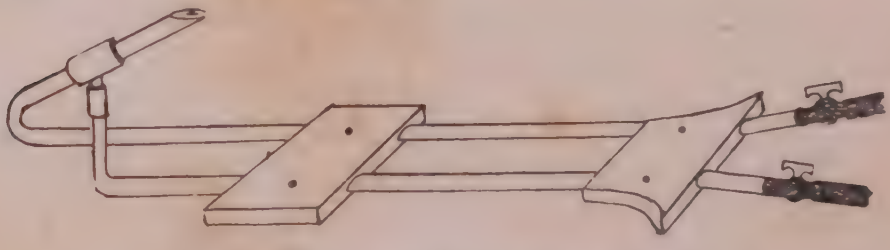


FIG. 25—OXY-ACETYLENE BURNER

6. A mixture of oxygen and acetylene under proper conditions burns with a non-luminous flame, and is capable of producing a temperature of 5,000° F. With this temperature it is possible to cut through steel plates in a very few minutes.

6. Summary

1. *Occurrence*—Paraffin wells; refining; shale industry; origin of mineral oils.

2. *The Industry*—

Products: Cymogene, rhigolene, petroleum, ether, benzoline, benzene, petrol, kerosene, lubricating oils, paraffin wax, vaseline.

3. *Analysis of Petroleum*—

1. Burn and show carbon.
2. Show water formed.
3. Heat with CuO; get H_2O and CO_2; consist of C and H.

4. *Marsh Gas*—Refer to fire damp in mines; to Dalton collecting it from stagnant pools.

1. Prepare by heating sodium acetate with NaOH. Collect over water.
2. Burn—show carbon and water formed.
3. Explain safety-lamp. Show by gauze over Bunsen burner.
4. Explode with air or oxygen.

5. *Acetylene*—Talk about bicycle-lamp—house lighting, etc.

1. Prepare by water on calcium carbide.
2. Burn—show carbon and water.
3. Show use of burner with small hole—luminous.
4. Explode with air.
5. Oxyacetylene flame—cutting metals.

7. Results

(A) *Ideas*—

1. Fractional distillation.
2. Saturation and stability.

(B) *Substances*—

1. Hydrocarbons of various series.
2. Methane.
3. Acetylene.

CHAPTER XI

ALCOHOL—VINEGAR

1. Natural Occurrence

Alcohol, because it occurs naturally whenever vegetable matter ferments or decays, has been known from earliest times. The Jews and Arabs were acquainted with fermented fruit juices of many kinds, and almost all native tribes when discovered have had their fermented root or fruit juices.

The ancient Arabic alchemists were searching for the elixir of life which was to make man immortal. This elixir they termed " the powder," and no doubt it was often discovered in some new substance which had potent healing properties, and for a time was supposed to give immortality. It was the panacea for all ills. To-day, on the bottles of medicine supplied by old-fashioned chemists, we still have written largely " The Powder," even when the substance inside is a liquid, and old-fashioned nurses still speak of all medicines as " powders." This is merely the continuance of this alchemist idea. Now the Arabic name for " The Powder " is " Al Kool," and we can imagine some Arab one day taking a draught of alcohol—feeling as he had never felt before and exclaiming " Al Kool." The real elixir had at last been found. What a delusion—if only he had lived to-day !

Mead, which was made from fermented honey, is perhaps the earliest drink of the English, whilst Potheen has been distilled in Ireland from very early times.

The fermentation of cereals for the production of beers was at first peculiar to England and Germany, and was developed during the seventeenth century.

2. Fermentation

Fermentation by means of small organisms such as those contained in yeast is necessary to the production of beer. Prior to 1857 chemists had divided views on the subject. Organisms were little understood, and their action not at all. Berzelius considered the fermenting process a catalytic reaction in which the ferment took no real part affecting its own change. Liebig regarded a ferment as an unstable substance, giving rise to alcohol by reaction, with certain fruits and cereals.

In 1857 Pasteur made a real study of the process of fermentation, and declared that there could be no fermentation without life. He observed that all ferments were living organisms, and that these acted on sugar or starch, digesting them and depositing alcohol. This theory gradually gained ground, and was generally accepted until 1897, when Buchner showed that life was not essential to fermentation. He proved that the living organism secreted a chemical substance, which was capable, apart from the organism, of producing alcohol from sugars and starch. These chemical substances are known as enzymes, and there are many of them known. The word itself means "out of yeast," the first one being produced from yeast. In fact, yeast produces several. The action of the chief enzymes in fermenting is shown below:

$$\underset{\text{(cane sugar)}}{\text{Sucrose } C_{12}H_{22}O_{11}} + \underset{\text{(in yeast)}}{\text{Invertase}} \longrightarrow \underset{C_6H_{12}O_6}{\text{Glucose}} + \underset{C_6H_{12}O_6}{\text{Fructose.}}$$

$$\text{Glucose } C_6H_{12}O_6 + \underset{\text{(in yeast)}}{\text{Zymase}} \longrightarrow \underset{C_2H_5OH}{\text{Alcohol.}}$$

Starch + Diastase (in malt) $\longrightarrow$ Maltose.
$C_6H_{10}O_5$ $C_6H_{11}O_5$

Maltose + Maltase (in malt) $\longrightarrow$ Glucose.
$C_6H_{11}O_5$ $C_6H_{12}O_6$

3. Experimental

1. Prepare alcohol by yeast on a solution of ordinary sugar.

Take a warm solution of sugar and add yeast. Leave at a temperature of 80° F. for two or three days and note the production of gas.

Carry out the experiment more quickly by heating the flask with a Bunsen burner. Lead off the gas and pass into lime-water. The lime-water is turned milky, showing the gas is carbon dioxide. Now connect with a condenser, and, keeping the temperature inside the flask below 100° C., continue to heat and collect the distillate. Test by smell and taste. A mixture of alcohol and water is produced.

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2.$$

2. Take some beer in a flask and connect to it a long glass tube 5 feet in length. Now heat the flask till it boils. Water and alcohol come off in the form of vapour, but the tube, which acts as an air condenser, condenses the water, and the alcohol can be made to burn at the top of the tube.

3. Heat some whisky or brandy in a beaker and burn the alcohol coming off. Refer to the burning of brandy over plum puddings.

4. Take some grapes and bruise them. Allow them to stand for several days. Note that fermentation has taken place. The grape skin contains its own ferment, which acts upon the glucose or grape sugar.

4. Commercial Processes

Alcohol is the general name for a whole series of compounds, the most common of which is ethyl alcohol, or spirits of wine, contained in most beverages. All the alcohols are poisonous in certain degrees, and capable of acting as stimulants. When pure they are extremely dangerous, if taken into the human system. Ordinary alcohol has many other uses than that of taking part in the production of beverages. Medicinally it is used as a preservative, and for hardening the skin. It also is a great solvent, dissolving readily such things as iodine, and thus producing the ordinary liniment, or lotion, used in first dressings. It is used largely in the preserving of specimens in museums, and in the form of methylated spirit as a fuel.

Methylated spirit is degraded alcohol prepared in an undrinkable state, so that it can be sold duty free. To do this, mineral and vegetable naphthas (wood spirit) are added. Even this does not prevent some people from drinking it, and during the war, when whisky was scarce, the quantity of methylated spirit drunk rose enormously. To stop this other impurities have been added. The drinking of methylated spirit causes an affection of the eyes leading to blindness.

There are three classes of beverages.

(*a*) Beers.
(*b*) Spirits.
(*c*) Wines.

1. *Beers* are prepared from cereals, chiefly barley. The first process is the manufacture of malt, which is carried out in a kiln. Barley is spread on a floor and water sprinkled on it. The temperature is kept even by fires on the floor below, and the barley occasionally raked over.

Gradually it begins to sprout with the formation of maltase, maltose, and diastase.

This malt is then taken and treated with yeast. Complete fermentation is not allowed, and in beer a certain amount of dextrin or gum is present. This gives the colour to beer. Flavouring is added, usually by hops, which give a bitter taste. Beer contains anything from 3 per cent. to 10 per cent. of alcohol.

2. *Spirits* are merely distilled beers. Whisky is made from malted barley, and is distilled so as to give about 50 per cent. alcohol. It is then placed in casks to mature, and this has an important effect on the flavour. In the production of alcohol a certain number of other substances are formed, especially fusel oils, which are higher alcohols (C_4H_9OH and $C_5H_{11}OH$). These are undesirable in the beverage, and if present give rise to serious headaches; but they are nearly always present in whisky, and can be detected at the bottom of the bottle if it is allowed to stand. Many a person has received a good dose of them when draining a bottle of whisky which has never been shaken.

The taste of whisky and most beverages depends, not on the presence of alcohol, but on that of various other bodies in very minute quantities. These bodies are known as esters, and are present in all fruits, giving each its distinct taste.

Brandy is made by distilling wine. Some brandy is made from cherries and known as cherry-brandy.

Gin is sometimes made from the starch of potatoes, fermented, then distilled; and most gin is finally redistilled with juniper berries.

Rum is made by fermenting molasses, then distilling the result.

3. *Wines* are made by the fermentation of fruit juices by enzymes on the fruit skin. The fruit is first crushed in a press—in some countries still by the treading of naked

feet—and then allowed to ferment. The wine is run off and placed in casks to mature, then bottled.

Sparkling wines, like champagne, contain carbon dioxide. Wines contain from 9 per cent. up to 30 per cent. alcohol.

4. *Liqueurs* (such as green chartreuse, benedictine, etc.), were mostly evolved in the monasteries, though some are the result of modern invention. They are mostly the result of distilling alcoholic beverages with fruits, roots, herbs, and flavouring material, such as peppermint, cashew bark, etc.

5. *Fusel oils* are a valuable by-product, as they are much used for fruit colouring and flavouring.

6. The distillation of wood gives rise to another alcohol called methyl alcohol (CH_3OH). When a mixture of this alcohol and air is passed over heated copper a substance known as formaldehyde is produced. This, when dissolved in water, gives us formalin, a very powerful disinfectant.

$$2CH_3OH + O_2 \longrightarrow 2CH_2O + 2H_2O.$$

7. *Absolute alcohol* is prepared from the products of fermentation by fractional distillation. It is never obtained absolutely free from water, about ·2 per cent. being present. It is required in scientific work and can be obtained duty free by authorized laboratories. Alcohol has a peculiar hardening property on foods, as can be shown by leaving sugar or bread immersed in it.

In the near future we may see the production of alcohol on a large scale from wood fibre by destructive distillation, and there is no reason why coal tar should not also be made to produce alcohol.

5. Vinegar

Vinegar is produced by the souring of wines or beers by minute organisms. Allow some wine or beer to be ex-

posed to the air for several days and note its sour character. This is due to the formation of acetic acid.

$$C_2H_5OH + O_2 \longrightarrow CH_3COOH + H_2O.$$

Commercially vinegar is prepared from cider, which itself is the result of fermenting apple-juice.

Vinegar which already contains the organisms is sprayed on wood shavings in a cask, and cider is put in by a spray from the top. Air is introduced, and the process goes on as the cider trickles down over the shavings. The vinegar is drawn off at the bottom.

Malt vinegar is prepared from malt and sugar vinegar from sugar.

White vinegar is made from pure distilled alcohol. It leaves no residue on evaporation.

The acidity of vinegar can be shown by litmus.

If vinegar is distilled more or less pure acetic acid can be formed.

6. Summary

1. *Natural Occurrence*—Refer to Arabic name, "Al kool"=the powder. Decomposition of organic products; beer; fermentation.

2. *Fermentation*—Prior to 1857 divided views. Berzelius described action as catalytic. Liebig regarded ferment as unstable substance. 1857, Pasteur showed "No fermentation without life." 1897, Buchner showed not due to the organism, but to a chemical secreted by it—enzymes (out of yeast).

3. *Experimental*—

1. Prepare alcohol by yeast on sugar.
2. Prepare alcohol from beer.
3. Burn alcohol from brandy.
4. Fermenting of grapes.

4. *Commercial Processes*—

1. Uses of alcohol.
2. Methylated spirit.
3. Three classes—beers, spirits, wines.
4. Liqueurs.
5. Formalin.
6. Absolute alcohol.

5. *Vinegar*—

1. Cider exposed gives vinegar. Alcohol oxidized by organism.
2. Manufacture: vinegar sprayed on wood shavings in a cask and hard cider put in; air admitted.
3. Show vinegar is acid.
4. Distil vinegar and get acetic acid, CH_3COOH.

7. Results

(A) *Ideas*—

1. Fermentation.
2. Enzyme and bacteria action.

(B) *Substances*—

1. Ethyl alcohol.
2. Methyl alcohol.
3. Acetic acid.
4. Formalin.

CHAPTER XII

SOAP—GLYCERINE

1. History

The use of soap, as we understand it, is probably not older than the time of the Romans. Although there are frequent Biblical references to soap, the Hebrew word "borith" so translated merely means herb, and shows that the Jews were in the habit of using special herbs containing potash (potassium salts) for cleansing purposes. The word potash refers to the ashes left in pots when vegetable matter is burnt. This ash contains a certain quantity of potassium hydrate, or caustic potash, now used in making soap.

The practice of the Hebrews of throwing ashes over their heads and sprinkling ashes on certain places is usually considered to be at least not a cleanly one, but, in fact, it was in itself a cleansing action, for the ashes were "pot-ashes," which have a distinct cleansing value.

Not only did the Jews understand the use of vegetable ashes as cleansers, but they were also acquainted with a mineral known as "Fuller" or "Fuller's earth," now used by old-fashioned nurses in the cleansing of babies, and employed in the manufacture of special soaps.

Both the Greek and Roman ladies washed their hair in water with pot-ashes, and Pliny speaks of a preparation being made from goat's grease and wood ashes. This would approximate to our lanoline soap.

In the ruins of Pompeii a complete soap factory was found, very much on the lines of our own factories. The

Romans probably introduced the making of some form of soap to this country, but it was not in general use until the sixteenth century. Then it was made in households and not in factories. In fact, until quite recent years it continued to be made in many country households, where the housewife kept her mutton and beef fat for the manufacture of soaps and candles. There are remote places to-day where farmers make their own soap.

By 1711 factories had been established, and the Government placed a tax on soap. This tax was removed only in 1853 by the efforts of Gladstone. The tax may be taken as testifying to the nation's contempt for the need of washing, or, on the other hand, it may have been a valuable source of revenue, owing to the people's desire for cleanliness at all costs.

2. Composition

Soap is a very simple compound, made from complex organic substances.

The two ingredients in the manufacture of soap are—(1) Oil, or fat; (2) alkali, and the by-product is glycerine. Fats and oils are merely the glycerine compounds of complex organic acids, and when boiled with an alkali the glycerine comes out and the metal of the alkali goes in.

The chief acids in the fats used for making soap are:

(A) Stearic acid, which can be written $HC_{18}H_{35}O_2$: the first hydrogen being replaceable by a metal. Now glycerine is $C_3H_5(OH)_3$, and the first part of it (C_3H_5) acts like a metal. Thus, the glycerine derivative of this acid is $C_3H_5(C_{18}H_{35}O_2)_3$, and is called stearin. Stearin is the main constituent of mutton fat. When this stearin is boiled with sodium hydrate, glycerine and sodium stearate are produced.

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3NaOH \longrightarrow C_3H_5(OH)_3 + 3NaC_{18}H_{35}O_2$$

(B) Oleic acid, $HC_{18}H_{33}O_2$. Olein is the glycerine derivative of this acid $C_3H_5(C_{18}H_{33}O_2)_3$, and is the chief constituent of olive oil. When this is boiled with sodium, hydrate glycerine and sodium oleate are produced.

$$C_3H_5(C_{18}H_{33}O_2)_3 + 3NaOH \longrightarrow C_3H_5(OH)_3 + 3NaC_{18}H_{33}O_2.$$

(C) Palmitic acid, $HC_{16}H_{31}O_2$. Palmitin is the glycerine derivative of this acid, and is found in palm oil, $C_3H_5(C_{16}H_{31}O_2)_3$. When this is boiled with NaOH, glycerine is again produced and the sodium salt of palmitic acid.

$$C_3H_5(C_{16}H_{33}O_2)_3 + 3NaOH \longrightarrow C_3H_5(OH)_3 + 3NaC_{16}H_{33}O_2.$$

The chief alkalies used are sodium and potassium hydrates, but other preparations are sometimes employed. If potassium hydrate is used, a soft soap is produced; and if sodium hydrate, a hard soap.

3. Commercial Process

The manufacturing processes of the different firms are much the same. Large vats or boilers, sometimes holding 500,000 pounds, are heated by steampipes passing through.

Into these the oil or melted fat is poured, and about one-quarter of the hydroxide necessary added. There is a danger in having excess of alkali, as it is injurious to the skin. In the case of soaps for laundry and household work, it does not matter so much as in the case of toilet soaps.

The stirring of the fat and alkali is done by forcing air or steam through the bottom of the vat. The whole process takes from two to four days, the remainder of the alkali being added as required.

When complete, common salt is added, and the mixture again heated. This causes the soap to rise to the top, and it is run off. It is then purified and mixed with any material desired, such as perfumes, borax, or sodium carbonate.

It then hardens in moulds, and is cut by machinery into long bars and stacked to dry. It is then further cut, stamped, and packed. The liquid remaining in the vats is called "spent lye," and the glycerine is removed from this by fractional distillation.

Special Soaps—*Soap powders* are usually made of anhydrous sodium carbonate mixed with ground soap. Such is "Dry soap."

Scouring soaps, such as Vim, contain a small percentage of ground soap, and a large amount of fine sand or ash.

Naphtha soaps contain a small percentage of mineral naphtha.

Transparent soaps, such as "Pears'," are made by dissolving the soap in methylated spirit and then distilling off the spirit. This makes the soap more durable.

Floating soaps contain bubbles of air.

A small quantity of soap can be made in a fairly large beaker by following the above directions. If the liquid mass is kept boiling no stirring is required.

4. Properties

1. Dissolve soap in water. It is fairly soluble in rain and distilled waters, and the solution is slightly alkaline, as there is partial decomposition, and NaOH (sodium hydrate) or KOH (potassium hydrate) is formed. Note the lather formed when this solution is stirred.

2. Add hydrochloric acid to this solution, and note that a white solid separates out. Examine this solid, and note that it is quite firm. The water now tastes salty. The solid is stearic acid.

$$NaC_{18}H_{35}O_2 + HCl \longrightarrow NaCl + HC_{18}H_{35}O_2.$$

3. Add calcium chloride to the solution, and note a white powdery substance separates out. Magnesium

chloride does the same. These substances are stearates. Again the water tastes salty.

$$2NaC_{18}H_{35}O_2 + CaCl_2 \longrightarrow 2NaCl + Ca(C_{18}H_{35}O_2)_2.$$

Hard waters contain calcium and magnesium chlorides, and these have to be got rid of before the soap can perform its work. (See Chapter IV.)

4. Dissolve soap in alcohol. It dissolves much more readily than in water. This is a convenient way of making a soap solution, and is much used in laboratory work, where soap solution is required for estimating the strength of other solutions and the hardness of various waters.

5. Glycerine

Glycerine is obtained as a by-product in the manufacture of both soap and candles, and is now more valuable than either the soap or the candles. It has enormous uses medicinally, but is more valuable because it forms the basis of many explosives. Hence during the war it was practically impossible to obtain glycerine.

1. *As a medicine* glycerine is used:

(*a*) As a lubricant for sore throats;
(*b*) In glycerine and rosewater for sore hands;
(*c*) For piles;
(*d*) As a stomach cleanser;

and it forms part of many medicines.

2. *Nitro-glycerine*—By the action of nitric acid on glycerine in the presence of strong sulphuric acid a compound known as nitro-glycerine is produced. The presence of sulphuric acid is necessary only to absorb the water produced.

$$C_3H_5(OH)_3 + 3HNO_3 \longrightarrow 3H_2O + C_3H_5(NO_3)_3$$

(nitro-glycerine)

The process is carried out at a low temperature, between 50° F. and 60° F. Nitro-glycerine can be made in this way in the laboratory, but the beaker must be kept cool.

Nitro-glycerine is a liquid and powerful explosive. It is extremely sensitive and explodes with very minute detonation or shock. It freezes at 40° F., and when in a solid state is particularly sensitive and may explode by scratching. As an explosive it is useless in its normal form; so it is prepared in different ways, of which the following are the chief:

(1) Dynamite. This consists of a mixture of nitro-glycerine and infusorial earth (Kieselguhr). It is quite a good explosive in dry places, but when wet the two substances separate. Several forms of dynamite are on the market, some of which overcome the disability of disintegration in the presence of moisture.

(2) Blasting gelatine. This consists of 93 per cent. of nitro-glycerine and 7 per cent. nitro-cotton. It is very safe and can be used equally well in wet places.

(3) Gelatine dynamite contains 80 per cent. blasting gelatine.

(4) Gelignite contains 60 per cent. blasting gelatine.

These explosives are largely used in mining operations.

6. Summary

1. *History*—Soap very old. Biblical references to Fuller as a cleanser.

2. *Composition*—(1) Fat or oil; (2) alkali. Refer to oils used in manufacture and to alkalies giving hard and soft soaps.

Stearin (fat) + Alkali —> Glycerine + Stearate

$C_3H_5(C_{18}H_{35}O_2)_3 + 3NaOH \rightarrow C_3H_5(OH)_3 + 3NaC_{18}H_{35}O_2$

3. *Commercial Process*—

1. Describe commercial process.
2. Make soap in a beaker.
3. Kinds of soap on market.

4. *Properties*—

1. Dissolve in water (soft).
2. Add HCl to solution, and get stearic acid as white solid.
3. Add $CaCl_2$ to solution, and get calcium stearate. Do same with magnesium chloride. Thus hard water and waste of soap.

5. *Glycerine*—Obtained in manufacture of soap and candles; used as medicine; taste. Used for nitro-glycerine.

1. Make a little nitro-glycerine by action of nitric acid and sulphuric acid on glycerine.

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(NO_3)_3 + 3H_2O.$$

2. Show dynamites and gelatine.
3. Explode some dynamite.

7. Results

(A) *Ideas*—

1. Solution of liquids—water and H_2SO_4.

(B) *Substances*—

1. Vegetable and animal fats.
2. Glycerine.
3. Calcium stearate.
4. Nitro-glycerine.

APPENDIX

THE USE OF FORMULÆ

From the days of the Greek philosophers the constitution of matter has always been a problem of philosophy, and this problem is fundamental to the study of chemistry. The ancient Greeks came to the conclusion that matter was formed of very small particles, called atoms, and this idea, with certain changes, has prevailed until to-day. Many philosophers, however, believed that matter was continuous, and it was probably because Newton supported the Atomic Theory that it finally became predominant.

It remained, however, for John Dalton, a Quaker schoolmaster, to show in 1808 how the vague theory of the Greeks could be made to explain the laws which govern chemical combination. Dalton's theory, clearly set out in "The New System of Chemistry," has been modified; but for over a century it has remained the basis of all chemical research. Whatever the future may have in store for this theory—even if it be entirely supplanted by a better one—it will always remain as the theory which bore fruit in practical results above all others in the realm of chemistry.

It is impossible in this work to enter into a full discussion of the Atomic and Molecular Theories. It will be sufficient to indicate the main results and thus provide an explanation to the formulæ used in the book.

An examination of substances will reveal the fact that

some are elementary—that is, they cannot be split up into any other substances which differ from themselves; and others are compound—that is, when treated in certain ways they yield other substances totally different from each other and from the original substance. The first of these classes is known as "Elements" and the second as "Compounds." Water is a compound, for in Chapter I. we discovered it consisted of two other substances, hydrogen and oxygen, both gases and both differing from each other and from water.

A compound must not be confused with a mixture. Air, we found, was a simple mixture of nitrogen and oxygen; for its properties are those of oxygen diluted by nitrogen, and it is possible to decrease the proportion of oxygen without destroying the qualities of air. One of the chief features of a compound, as we shall see, is that the proportions of the elements forming it are always constant.

It must not be thought that there are such things as absolute elements. Many substances formerly considered to be elements have been discovered to be compounds, and many of the substances to-day thought to be elements may in the future be split up into other elements. In fact, we may yet discover that all substances are made up of one primal substance.

There are, however, some seventy substances which have not yet been split up into more elemental substances, and these are denoted by symbols. Usually the symbol is the first letter of the name of the element, or it may be the first two letters, or the first and some other letter, or it may be derived from the Latin name for the element. Now, any portion of each element is made up of an infinite number of atoms. These atoms and the spaces between them are so small that they cannot be seen by the most powerful microscope. Atoms are supposed to have

weight, and the weight of every atom of a single substance is the same—that is, for example, the weight of an atom of iron is always constant. But an atom of any other substance has not the same weight as an atom of iron. Each substance has its own atomic weight. Now, it must not be imagined that these weights are real—they are only relative. Therefore, if we say the atomic weight of oxygen is 16, we do not mean that an atom of oxygen weighs 16 anything, but that *if* an atom of oxygen weighs, say, 16 grammes, then an atom of hydrogen weighs 1·008 grammes, and an atom of chlorine weighs 35·46 grammes. The following is a table of the chief elements, giving their symbols, an explanation where necessary, and their relative atomic weights.

Aluminium	Al	..	27·1	
Antimony	Sb	..	120·2	(From "Stibium.")
Argon	A	..	39·88	
Arsenic	As	..	74·96	
Barium	Ba	..	137·37	
Bismuth	Bi	..	208·0	
Boron	B	..	11·0	
Bromine	Br	..	79·92	
Cadmium	Cd	..	112·4	
Cæsium	Cs	..	132·81	
Calcium	Ca	..	40·07	
Carbon	C	..	12·0	
Cerium	Ce	..	140·25	
Chlorine	Cl	..	35·46	
Chromium	Cr	..	52·0	
Cobalt	Co	..	58·97	
Copper	Cu	..	63·57	(From "Cuprum.")
Fluorine	F	..	19·0	
Gold	Au	..	197·2	(From "Aurum.")
Helium	He	..	3·99	
Hydrogen	H	..	1·008	
Iodine	I	..	126·92	
Iridium	Ir	..	193·1	
Iron	Fe	..	55·84	(From "Ferrum.")
Krypton	Kr	..	82·92	
Lead	Pb	..	207·1	(From "Plumbum"; [*cf.* Plumber.)
Lithium	Li	..	6·94	
Magnesium	Mg	..	24·32	
Manganese	Mn	..	54·93	

Mercury	Hg	..	200·6	(From "Hydrargyrum.")
Nickel	Ni	..	58·68	
Nitrogen	N	..	14·01	
Oxygen	O	..	16·00	
Palladium	Pd	..	106·7	
Phosphorus	P	..	31·04	
Platinum	Pt	..	195·2	
Potassium	K	..	39·10	(From "Kalium"; *cf.* Kali.)
Radium	Ra	..	226·4	
Silicon	Si	..	28·3	
Silver	Ag	..	107·88	(From "Argentum.")
Sodium	Na	..	23 00	(From "Natrium.")
Strontium	Sr	..	87·63	
Sulphur	S	..	32·07	
Tin	Sn	..	119·0	(From "Stannum.")
Zinc	Zn	..	65·37	

It will be noticed that metals we usually call "heavy" have high atomic weights.

A study in the light of the Atomic Theory of the way in which elements combine to form compounds led to the formulation of three laws:

1. The law of fixed proportions.
2. The law of multiple proportions.
3. The law of reciprocal proportions.

1. *Law of Fixed Proportions*—Black and Lavoisier had noticed that *chemical compounds were formed by the combination of their elements in fixed proportions*, but it was Proust (1755–1826) who finally established the law.

If Dalton's theory is right that the ultimate particles or atoms of any one substance have the same weight, and if the atom is the smallest particle of matter capable of entering into chemical union, then it is clear why this law holds good. To take a concrete example from Chapter IV., we have the substance lime, which on decomposition yields calcium (a metal) and oxygen in the ratio of 40·07 to 16·00 by weight. Thus, one atom of calcium unites with one atom of oxygen, and we therefore write lime as CaO. Similarly, we write common salt as NaCl,

and on analysis it yields sodium and chlorine in the ratio of 23 and 35·46. These ratios are always found to be constant.

2. *The Law of Multiple Proportions*—This law was the result of work done by such men as Thomson, Berzelius, and Gay Lussac at the beginning of the nineteenth century. It states that: *If two or more elements form several compounds, the fixed proportions in which the elements combine together are in simple ratios to one another, and these ratios can be expressed by whole numbers.*

In Chapter III. a substance named sodium-per-oxide is mentioned, and is written Na_2O_2. Now, sodium forms two oxides with oxygen, and the other one is Na_2O. If these two oxides were analyzed it would be found that the first contained sodium and oxygen in the ratio 46 : 32 and the second in the ratio 46 : 16.

Thus, the ratio of the sodium in both compounds is 1 : 1, and that of the oxygen 2 : 1. It would be impossible to have a compound in which sodium and oxygen bore the ratio of 23 : 9·7, for instance. It is clear that these two elements can only combine in ratios which are formed by their atomic weights or multiples of their atomic weights. Thus, we never find chemical formulæ such as these—Cu_3O_4, Cu_4S_7, etc., but always such as CuO, which means one atom of oxygen is combined with one atom of copper; or H_2O, which means two atoms of hydrogen are combined with one atom of oxygen.

3. *The Law of Reciprocal Proportions* need not be considered here. Enough has been said to show that the atom is the chief feature in chemical combination.

A study of gases led to the conclusion that they always combined in volumes which bore simple relations to each other, which relations could be expressed by whole numbers. Thus, two volumes of hydrogen unite with one volume of oxygen to give two volumes of steam.

This was worked out by Gay Lussac, and clearly has some connection with Dalton's Theory; but, strange to say, Dalton rejected the findings of Gay Lussac. This may have been due to the fact that on Dalton's hypothesis alone the findings of Gay Lussac are not quite clear. What happens in the case of steam is—

2 vols. of H+1 vol. O=2 vols. of steam,

i.e.,

2 vols.+1 vol.=2 vols.;

and this, according to Dalton, would be—

2 atoms+1 atom=2 atoms.

Avogadro (1776–1856), Professor of Physics at Turin, completed the work which Dalton had begun. We may sum up his work as follows:

1. The molecule is the smallest particle of matter capable of separate existence.

2. The atom is the smallest particle of matter entering into chemical combination.

3. The molecule consists of two or more atoms. In the case of elements each molecule contains usually two atoms. Thus, a molecule of oxygen is expressed O_2. In the case of compounds the molecule may contain any number of atoms. Thus, a molecule of water contains three atoms, and is written H_2O; whilst a molecule of glycerine contains fourteen atoms, and is written $C_3H_5(OH)_3$.

4. When substances enter into combination they do so by molecules, but elements may change place between the molecules. Thus, in Chapter I. we have sodium acting on water and producing hydrogen and sodium hydrate, and we represented the reaction as follows:

$$2H_2O+Na_2 \longrightarrow 2NaOH+H_2.$$

i.e., 2 molecules of water + 1 molecule of sodium gives 2 molecules of sodium hydrate + 1 molecule of hydrogen.

5. All *gases* at the same temperature and pressure contain the same number of *molecules*. Gases are different from solids and liquids in this respect. In view of the theory of Avogadro, we may again examine water. It is found by experiment that—

2 vols. H + 1 vol. O = 2 vols. steam,

and this is easily explained now:

2 mols. H + 1 mol. O = 2 mols. steam,

so that we may write

$$2H_2 + O_2 \longrightarrow 2H_2O.$$

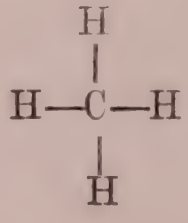
An examination of many carbon compounds led to a further study of how atoms were built up into the molecule—*i.e.*, an examination of the internal structure of the molecule. Various theories have been advanced, but it is impossible to enter into them here. It is only necessary to say that where a number of carbon atoms are joined together in one molecule, as, for instance, in benzene, C_6H_6, there are at least two possible ways in which the carbons may be linked together: (1) In a chain, thus:

C—C—C—C—C—C.

(2) In a ring, thus:

There are certain facts in chemistry which can only be understood by allowing these "ring compounds," and in Chapter X. some of these strange formulæ appear.

The theory of chemical combinations can be easily understood by regarding the whole as a battle of atoms, or perhaps of amorous duels fought for the possession of fair maids (other atoms). Each element has a certain fairly defined capacity for other elements—*e.g.*, an atom of carbon requires four atoms of hydrogen before it is really satisfied or saturated. The atom of carbon can, however, be satisfied with two atoms of oxygen. Thus, one atom of oxygen equals two atoms of hydrogen. We represent this capacity of carbon for hydrogen as shown:



Such a substance CH_4 (methane or marsh gas) is therefore a saturated substance—*i.e.*, it is not easily decomposed; in other words, it is stable. But a substance like C_2H_2 (acetylene) is not saturated, and under certain conditions is very unstable and even explosive.

This capacity of elements for each other is measured with respect to hydrogen and is called valency. Thus, carbon is tetra-valent and oxygen is di-valent.

These facts will serve to make clear the equations used in the book, and it is to be noted that there are chiefly two kinds of reactions represented by equations:

(1) *Simple*, where there is a mere splitting up of a compound; or a formation of a compound from other elements or compounds—

$$\left.\begin{array}{l} 2HgO \rightarrow Hg_2 + O_2 \\ CaO + CO_2 \rightarrow CaCO_3 \end{array}\right\} \text{Chapter II.}$$

(2) *Complex*, where elements change over from one compound to another—

$$2NaCl + MnO_2 + 2H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$ } Chapter V.

Here it will be seen that the atoms on both sides of the equation correspond, but their relative positions are different, some of the atoms having changed over.

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